V. N. Ipatieff

CATALYTIC REACTIONS AT HIGH PRESSURES AND TEMPERATURES

BY

VLADIMIR N. IPATIEFF

Member of Academy of Sciences, U.S.S.R., Doctor of Chemistry, University of St. Petersburg; Professor Emeritus, Artillery Academy, St. Petersburg.

Corresponding Member of Academy of Sciences, Göttingen; Doctor Honoris Causa, University of Munich, Honorary Member of German Chemical Society.

Doctor Honoris Causa, University of Strasbourg; Commander of the Legion of Honor.

Professor, Northwestern University; Director of Chemical Research, Universal Oil Products Company, Chicago, Illinois.

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This book is dedicated to the memory
of my dear mother
ANNA DIMITRIEVNA IPATIEFF

FOREWORD

This book primarily is a collection and review of my researches in the field of catalysis during the past thirty-five years. The task of writing it was undertaken because I believed that a collection of these researches would be of interest and much of my published work is otherwise inaccessible.

This book is my chemical autobiography. For that reason, no attempt was made to collect the literature or to include the work of others except in special cases where it was desirable to emphasize and develop certain features, or where it was considered to have a direct bearing upon my own researches.

I have devoted my entire scientific lifetime to the exploration of this little known and difficult field. In the interests of the history of catalysis, it is important that the correct significance be placed upon my investigations.

This has not always been done. A number of authors of monographs on catalysis have not referred at all to my original publications. However, Marek in his book, "The Catalytic Oxidation of Organic Compounds in the Vapor Phase" (1932) placed the true value upon my investigations of the catalytic decomposition of alcohols under the influence of specific catalysts.

In some cases, my work has been criticized. For instance, one specialist in catalysis wrote: "The application of the expensive and dangerous apparatus in not compensated by the advantages of the Ipatieff method."

Today, all workers in catalysis realize the importance of high pressure. The dangers incident to its use have been greatly exaggerated. My co-workers and I, since 1903, have safely made several thousand high pressure experiments in bombs of my own design. My method of bomb closure has been widely adopted.

Only by application of high pressure is it possible to hydrogenate completely and obtain pure products (free from traces of starting material). At the present time, cyclohexane, tetralin, decalin, and numerous other products are produced commercially by my high pressure methods.

I was the first to demonstrate the possibility of hydrogenating in the liquid phase (the hydrogenation of liquid hydrocarbons and of the salts of unsaturated acids). These results would be impossible according to the theory and method of Sabatier.

The above title was given to the book since the dominant feature is pressure and I am the pioneer in the use of pressure in chemical reactions. However, many reactions are described which were made at ordinary pressure.

My investigations during the past five years have resulted in the development of certain hypotheses applicable to the catalytic reactions of dehydration, polymerization, alkylation, and isomerization. Some of these results are published for the first time in this book.

The reader will find numerous studies which I did not finish because of the conditions under which I worked. These unsolved problems have not lost their interest and I shall feel fully compensated for this publication if it inspires others to further work in this field.

I wish to express my deep gratitude to my beloved wife, Barbara, to my life-long friend Professor Willstaetter, to Mr. Hiram Halle and the Universal Oil Products Company for material support, to Drs. Gustav Egloff, A. v. Grosse, and Jacques Morrell for helpful suggestions, and to Drs. S. Berkman, B. B. Corson, and R. E. Schaad for translating and correcting the book.

VLADIMIR IPATIEFF

July, 1935

VLADIMIR IPATIEFF

By Professor R. Willstaetter (München)

Die Jugendarbeiten von Ipatieff wurzeln in den grossen Traditionen der russischen Chemiker. Sie liefern schöne Beiträge zur Kenntnis der Kohlenwasserstoffe, insbesondere der Additionsreaktionen ungesättigter Kohlenwasserstoffe. Schon hier, namentlich in den Untersuchungen über die Konstitution und die Synthese des Isoprens vom Jahre 1897 tritt die Selbständigkeit und Originalität in der Wahl und Behandlung grosser Probleme hervor, die Jahrzehnte später in der Entwicklung der organischen Chemie eine Rolle spielten.

In noch höherem Masse gilt dies für die aus sehr zahlreichen und gründlichen Untersuchungen bestehende Hauptgruppe des Lebenswerkes von Ipatieff, dass darin neue Probleme, neue Wege, neue Methoden eröffnet werden und zwar von solcher Tragweite, dass darin die moderne Entwicklung der anorganischen und organschen technischen Chemie vorgeahnt und angebahnt erscheint. Die Arbeiten von Ipatieff über "Pyrogenetische Kontaktreaktionen organischer Verbindungen" und über "Katalytische Hydrierungen" sind nämlich durch zwei Umstände ausgezeichnet: durch Einführung sehr hoher Drucke und durch die Wahl und Variationen der Katalysatoren.

Heute wird als eine Hauptaufgabe der Chemie die Erforschung des Wesens, der Wirkungsweise und die Konstitution der organischen Katalysatoren, der Fermente, deutlich. Und in der praktischen Chemie hat die Ausgestaltung der Lehre von den anorganischen Katalysatoren, die Steigerung ihres Leistungsvermögens und ihre Ausbildung für spezifische Reaktionslenkungen in den technischen Methoden der Ammoniaksynthese, der Salpetersäuregewinnung, der Hydrierung von Kohlenoxyd, der Gewinnung von Benzinen aus Kohle, ihre überragende Bedeutung erwiesen. Der zweite wesentliche Umstand in den Arbeiten von Ipatieff über Katalyse und zwar schon in den ersten Jahren dieses Jahrhunderts war die Anwendung sehr hoher Drucke. Dieses Prinzip ist in den letzten zwei Jahrzehnten

seit dem Erfolg der Haber'schen Ammoniaksynthese immer mehr zu einer beherrschenden Methode für grossindustrielle Prozesse geworden.

Diese neue Prinzipien sind in den Untersuchungen von Ipatieff ausserordentlich früh angewandt worden. Ipatieff zählt daher zu den grossen Anregern und Förderern der Chemie unserer Zeit.

TRANSLATION

Ipatieff's early work is rooted in the great traditions of the Russian chemists. He made excellent contributions to the knowledge of hydrocarbons, especially of the addition reactions of unsaturated hydrocarbons. Independence and originality in the choice and treatment of broad research problems, which decades later were to play a part in the development of organic chemistry, were apparent in his early work on the constitution and synthesis of isopropene in 1897.

Indeed, independence and originality are manifest throughout the many fundamental investigations in the field which was his life work. His problems and his methods of attack seem to foreshadow and to prepare the way for the modern developments of organic and inorganic industrial chemistry. The works of Ipatieff on "Pyrogenetic Contact Reactions of Organic Compounds" and "Catalytic Hydrogenation" are distinguished by two particular features: the choice and variety of catalysts and the introduction of very high pressures.

Today one of the major problems of chemistry is the investigation of the nature, the mode of reaction, and the structure of the organic catalysts, the ferments. Of great importance in applied chemistry is the study of inorganic catalysts, increasing their effectiveness and developing suitable catalysts for specific reactions such as the synthesis of ammonia, the manufacture of nitric acid, the hydrogenation of carbon monoxide, and the production of liquid fuels from coal. The second important feature of Ipatieff's study of catalysis, applied in the first years of the century, was the use of very high pressures. In the last two decades, since the success of the Haber ammonia synthesis, high pressures have become increasingly important in industrial processes.

These new principles were used very early in Ipatieff's investigations. Ipatieff, therefore, is one of the great pioneers in the chemistry of our day.

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INTRODUCTION

At the beginning of the 20th century very little study from the chemical viewpoint had been given to pyrogenetic reactions of decomposition of organic compounds.

In spite of the fact that the dry distillation of organic compounds was so important in the production of many substances, pyrogenetic reactions had not been investigated with the completeness necessary for clarification of their course when yielding various products. Probably the variety of products obtained was the chief reason that pyrogenetic processes did not receive more scientific investigation.

Almost all investigators held a definite opinion that at high temperatures (above 300–400°) the molecules of an organic compound would decompose in various, probably selective directions, and that the resulting fragments of molecules would combine with each other to form various compounds. In such pyrogenetic processes different reactions of decomposition, polymerization, and condensation could be observed, and their sequence followed. To explain the formation of this or that product seemed to be a very difficult matter, and in some cases even impossible. It should be noticed that investigators of pyrogenetic reactions paid very little attention to the temperature at which the process occurred and nobody attached much significance to the material of the vessel in which the pyrolysis was conducted. After making numerous investigations on organic substances at high temperatures and pressures during the first third of the 20th century, it became obvious to us why pyrogenetic processes could not attract the minds of chemists. Primarily a study of the pyrolysis of the simplest organic compounds was necessary and observations had to be made of the laws of their decomposition and the course of other concurrent reactions that can take place.

The first significant investigation of pyrogenetic reactions was made by Berthelot, who showed in a series of works the most interesting pyrogenetic syntheses of various hydrocarbons. But in the pyrogenetic reactions studied by Berthelot as well as by others, the main effect was ascribed to the temperature (thus these reactions were named pyrogenetic) and no attention at all was paid to many other conditions of the experiments.

Thus, for example, indications are found in the literature that even before the time of Berthelot ethyl alcohol had been subjected to pyrogenetic decomposition by passing it through a glowing tube. Different writers stated that they had used tubes made of various materials: glass, porcelain, glass containing pumice, etc., but no one attached significance to the latter circumstance, nor accurately measured the temperature at which the process was conducted. Therefore, it is understandable why the various writers obtained different results. Deyman in describing the decomposition of ethyl alcohol in a glass tube indicated that a gas was formed which burned with a weakly luminous flame. Marchand obtained carbon, aldehydes, and gas by leading vapors of ethyl alcohol through a glowing porcelain tube packed with pieces of pumice. Sassure obtained aldehyde among the products of decomposition of ethyl alcohol. At the end of the 18th century, four Dutch chemists, Deyman, Van Trooswyk, Lauwrenberg, and Bondt observed the decomposition of ethyl alcohol by kaolin into gases in which ethylene predominated. Finally Thiele in 1898, in studying the pyrogenetic decomposition of isoamyl alcohol with the object of obtaining butadiene, employed an iron tube merely for the safety of the experiment.

However, in spite of the variety of results obtained by the decomposition of one of the simplest organic substances under the influence of high temperature, nobody was interested in finding the real reason for these variations or in studying quantitatively the products of the reactions.

At this time the frequently used decomposition of alcohols by zinc chloride at a temperature of about 300° was considered as a pyrogenetic reaction, and it was assumed that even at this temperature a complete decomposition of the molecule took place. The fact that various products resulted was considered possible only by the supposition that the molecule of alcohol split into several fragments.

If attention be paid as to how this reaction has been conducted by various writers it is seen that even the temperature of the reaction was not measured accurately, no attention was given to the question of what became of the zinc chloride, and no significance was attached to the walls of the vessel in which these pyrogenetic reactions occurred.

Besides, at that time the decomposition temperatures of organic compounds were not even known approximately, as only the general action of heat had been observed, for example, the behavior of alcohol vapor in a glowing glass tube. Therefore, it is understandable that it was then out of the question to observe the action of catalysts upon the course of the decomposition of carbon compounds at high temperatures.

Actually in order to solve the question as to whether catalysis takes place in the decomposition of organic compounds it is extremely important to know the temperature a certain splitting of the molecule under the influence of heat alone and also the temperature of the same decomposition of the molecule when taking place in presence of certain substances. If the substance introduced strongly decreases the temperature of the decomposition of the organic compounds in a certain direction, and if the substance itself remains unchanged, the latter will be a catalyst and consequently the decomposition reaction will be catalytic.

Up to the beginning of the 20th century no one had succeeded in observing that at high temperatures (above 300°, and especially at 500–600°) a catalyst could influence the course of decomposition of an organic substance and force the decomposition to go in a certain direction only.

In the year 1900, I was the first to answer this question positively in a study of the pyrogenetic decomposition of isoamyl alcohol at 520–540°. The alcohol vapors were passed through an iron tube in order to obtain butadiene and a study was made of the liquid products of decomposition which had not been investigated previously.

The main product of the reaction was isovaleric aldehyde mixed with unreacted alcohol. These data immediately drew my attention to the factor which had not been considered by other investigators as playing any part in the pyrogenetic reactions of organic compounds, namely the material of the vessel in which the decomposition of the organic substance took place which might play the part of a catalyst. From the beginning of my work on pyrogenetic reactions, it was apparent that I was dealing with contact phenomena, because of a certain difference in the products of decomposition of organic substance which had been noticed depending upon the material of the tube in which the pyrogenetic reaction occurred. Also I was able to guide the reaction in a definite direction by correct choice of catalyst. Of course it is not possible to study accurately the decomposition reaction of organic compounds occurring under the influence of heat alone, without the influence of foreign substances, because the walls of the reaction vessel always influence the course of the reaction, although possibly only to a small extent. At the beginning of the investigation of reactions at high temperatures these reactions were divided into two classes: the simple pyrogenetic and the catalytic pyrogenetic; the latter reaction indicated application of catalysts which strongly decrease the temperature of decomposition and force the molecule to decompose in a definite direction with the formation of definite products. During the first two years (1900–1902) I was the first to establish definitely that alcohols might be decomposed in two ways under the influence of catalysts at high temperatures: (1) With the formation of almost pure aldehyde or ketone and hydrogen under the influence of zinc, iron, brass, etc., and oxides of the same metals (zinc oxide, iron oxide, copper oxide, etc.),

$$RCH_2OH \rightarrow H_2 + RCOH$$
$$R\text{—}CHOH\text{—}R \rightarrow H_2 + R\text{—}CO\text{—}R$$

and (2) with the formation of ethylene and water only under the influence of alumina and kaolin:

$$RCH_2OH \rightarrow H_2O + C_2H_4$$

In the next year (1903) a third kind of decomposition of ethyl alcohol was discovered by which *butadiene* (divinyl) was formed under the influence of powdered aluminum and alumina.

$$2CH_3CH_2OH \rightarrow 2H_2 + H_2O + CH_2{=}CHCH{=}CH_2$$

When the influence of catalysts upon the course of the decomposition of organic compounds was established with certainty, I gave my attention at once to the necessity of investigating these catalytic reactions in a closed space in order to study them from the viewpoint of chemical kinetics and to solve the question of their reversibility. Besides it was extremely interesting to study the influence of the new factor, pressure, upon the course of catalytic processes.

The study of catalytic reactions at high temperatures and pressures encountered great difficulties at this time (1901–1903) because it was impossible to find an autoclave in Russia or abroad which would permit work at 400–500° under pressure up to 400 atmospheres. The autoclaves of that time made for pressures of 25 to 50 atmospheres could not be used with safety even for such small pressures. By the end of 1903, after a series of attempts, such an apparatus, or a bomb, was constructed. It had such a safe closure that the investigation of a variety of catalytic reactions at high temperatures and pressures could be safely made. In this bomb several thousand experiments were carried out. For laboratory work the closure proposed seems to be the safest and most satisfactory.

The study of catalytic reactions under pressure at high temperatures immediately gave very valuable results. First it was shown that many catalytic reactions are reversible at high temperatures and that it is possible to observe the intermediate phases of the reaction although such observations are impossible at ordinary pressure. Under pressure the process of hydrogenation proceeds with much greater velocity and it is possible to hydrogenate organic compounds which decompose under ordinary pressure at the necessary temperature. For the first time it was ascertained that hydrogenation proceeds in both liquid and solid phases (hydrogenation of salts), and in aqueous solutions. The introduction of the pressure factor into catalytic reactions at high temperature made hydrogenation possible on a plant scale. Besides this it was possible to investigate many reactions from a kinetic standpoint because of the possibility of following the course of the reaction by pressure readings on the manometer. Thanks to this method for the study of reactions of organic compounds under pressure, it was possible to investigate the effects of temperature, pressure, and catalyst in very important reactions, which were checked later by other workers and operated on a plant scale for obtaining products valuable to the chemical industry. During the period 1903 to 1914, I studied the following reactions under pressure:

(1) Decomposition of organic compounds with and without hydrogen in the presence and absence of catalysts in a bomb with iron walls or in autoclave made of phosphor bronze; (2) Hydro-

genation of various classes of organic compounds in the presence of various catalysts, especially of metal oxides; (3) Dehydration of aliphatic and cyclic alcohols; (4) Isomerization; (5) Polymerization of olefins; (6) Destructive hydrogenation.

The latter work (6) was carried out in 1926. Because of other work and the Revolution I was forced to discontinue my scientific activity from 1914 to 1922. During the World War, from 1914 to 1917, I was engaged in directing the Chemical Industry in providing munitions, gas, and gas-masks.

In 1910 while studying the hydrogenation of organic compounds, I noticed a very important fact that hydrogenation occurs especially favorably and at a lower temperature when a certain amount of another substance is added to the catalyst. This substance, often called the promoter, helps the reaction, although it is not able to catalyze the hydrogenation alone. Its help comes through a catalytic side reaction which it produces. It was found possible to explain such reactions by the joint action of catalysts and to predict when substances might be promoters for hydrogenation.[1] However, it was known a long time ago that the addition of certain substances in catalytic reactions accelerates the process, although nothing had been described on hydrogenation processes at high temperatures and pressures either in the literature or in the patents up to 1910. Consequently Prof. Taylor and Prof. Rideal in their book on catalysis ascribe to me the honor of the discovery of the influence of promoters upon the action of catalysts. As is known at the present time, catalytic reactions have to be performed in a great number of cases under the joint action of catalysts.

At the beginning of the discovery of catalytic reactions in the decomposition of alcohols (1901), I proposed an hypothesis concerning the explanation of these reactions under the influence of metals and their oxides. This hypothesis was discussed superficially by Sabatier and Senderens in the pages of "Comptes Rendus" in 1903, but strange to say, my hypothesis was not even mentioned in Sabatier's book, "La Catalyse dans la Chimie Organique."

First, the hypothesis made possible the prediction of the ways in which metals and their oxides might be good catalysts for the aldehyde decomposition of alcohols. Secondly, this hypothesis also led me to the discovery of alumina as catalyst for dehydration of alcohols, and furthermore, to the discovery of mixed catalysts and the effects of promoters. This hypothesis which led to the prediction of new facts and permitted the simplest explanation of catalytic processes from the chemical viewpoint should merit attention. Also I feel justified in indicating the date of its appearance in science.

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[1] This discovery which I made in 1909 and 1910 and published in 1910 in the Ber. Deut. Chem. Ges. drew the attention of Prof. Paal at once, who in the next article in the Berichte D. Ch. G. indicates the importance of this observation and its application in his work on hydrogenation according to this method.

Moreover this seems to be warranted because in many monographs[1] as well as in publications by various writers on the theory of catalysis, a definite indication may be found in support of the fact that metal oxides and water play an essential part in catalytic reactions of hydrogenation and dehydrogenation. On the other hand, the works of Langmuir prove that the surfaces of metals are covered by thin oxide films, which according to my hypothesis play an essential part in catalytic reactions.

The same hypothesis led me also to the explanation of the phenomenon of polymerization by the action of various catalysts and the discovery of new catalysts for the alkylation by olefins of a whole series of organic compounds: the paraffin, naphthene, and aromatic hydrocarbons, as well as phenols and other substances.

From 1923 to 1933 when circumstances again favored the continuation of my scientific activities in the laboratory of the Academy of Science and later in the Institute of High Pressure established by me, destructive hydrogenation and condensation under the action of mixed catalysts were studied. More recently my attention was centered chiefly on the study of polymerization of olefins and the alkylation of various classes of organic compounds.[2] This most recent period of my scientific work was facilitated by the coöperation of many associates, and I was therefore able to organize the work on a larger scale than was possible before 1914.

In 1908, I applied high pressure methods to the study of reactions of inorganic compounds. At the beginning of the investigation with aqueous solutions of metallic salts, it was observed that pressure and temperature had an enormous effect upon the course of the reaction. I was the first to succeed in separating

[1] H. Wolbing, "Hydrierung," 1926, p. 97, Kohle-Koks-Teer, Vol. 8.

[2] Universal Oil Prod. Co., Riverside, Ill.

metals such as copper, nickel, cobalt, tungsten, lead, cadmium, zinc, etc., from their solutions by means of hydrogen.

Thanks to the investigation of reactions of inorganic compounds under pressure it was possible to separate metallic oxides, double salts, and silicates in excellently formed crystals and to effect the formation of kaolin.

The study of oxidation processes with water under pressure led to the discovery of the oxidation of phosphorus by water with formation of phosphoric acid and pure hydrogen as the final products. The material accumulated in recent times concerning the reactions of inorganic compounds is so large that its systemization and description requires a special monograph which I hope to write in collaboration with my son V. Ipatieff, Jr., who has done much interesting work in this field.

The study of catalytic reactions in organic chemistry at various temperatures develops more and more, but much more work is still necessary before we can explain the chemical actions of catalysts and be able, by using contemporary physico-chemical methods, to clear up the relationship which exists between the physical and chemical properties of a catalyst and the properties of the substances catalyzed.

The study of catalytic reactions of organic substances at high temperatures and pressures is interesting also because, in all probability, it will lead to the explanation of many processes which occur with organic compounds in the depths of the earth. This concerns also the inorganic compounds. The pressure, temperature, and the character of the substances with which the decomposed organic substance comes in contact must influence the course of its decomposition and consequently various products must be obtained. It is possible that the investigation of catalytic reactions occurring at high temperatures and pressures will give the proper material for the clarification of the question of the origin of petroleum and will offer an explanation of various properties possessed by the different kinds of petroleum found in nature.

CATALYTIC REACTIONS AT HIGH PRESSURES AND TEMPERATURES

CATALYTIC REACTIONS AT HIGH PRESSURES AND TEMPERATURES

CHAPTER I

DEHYDROGENATION

CATALYTIC DECOMPOSITION OF ALCOHOLS AT ORDINARY PRESSURE

In 1900 I began the study of the catalytic reactions of organic substances at high temperature and at the January (1901) meeting of the Russian Physical Chemical Society gave my first paper on "Pyrogenetic Reactions of Organic Compounds." There I showed definitely that contact phenomena take place in the decomposition of alcohol because the products obtained depended upon the tubes used for pyrolysis. No previous investigation had indicated the possibility of introducing catalysts to influence or direct the course of decomposition of organic substances at high temperatures.

Some earlier investigators had made a few observations on the decomposition of alcohol. Thus Deuman [1] found that ethyl alcohol vapor when passed through a glowing tube formed a gas which burned with a slightly luminous flame. Marchand [2] obtained aldehyde, gas, and carbon by leading ethyl alcohol through a glowing porcelain tube packed with pieces of pumice. In addition Berthelot [3] detected small amounts of aldehyde and hydrogen in the products resulting from passage of alcohol through a glowing porcelain tube packed with pumice. Sassure,[1] however, did not observe the formation of aldehyde in similar experiments. Considering the different products obtained in these early investigations it could not be concluded that alcohol may decompose into aldehyde and hydrogen under the sole influence of heat. Carbon which is always formed from alcohol at high temperature in the presence of pumice might act as a catalyst for the dehydrogenation of alcohol. The slight formation of aldehyde might be ascribed to oxidation of alcohol by oxygen of the air present in the apparatus at the start of the experiment. Of course, ethylene formation by decomposition of alcohol was known long before the time of Berthelot from the study of Diemann, van Troostwyk, Lauwrenburg, and Bondt.[1] These Dutch chemists showed that at high temperature and in the presence of kaolin ethyl alcohol decomposes into gas, predominately ethylene.

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[1] Gmelin, Handbuch org. Chem., Vierte Auflage, 1848, IV, p. 551.

[2] Marchand, J. prakt. Chem., *15*, 7 (1838).

[3] Berthelot, Les Carbures d'Hydrogene, *2*, 202 (1901).

Although attempts were made to write the equation [2] for the decomposition of alcohol at high temperature, no attention was paid to the influence of catalysts and, as a matter of fact, before the publication of my results in 1901 nobody could draw such conclusions concerning the course of decomposition of ethyl alcohol. Up to 1900 none of the investigators had visualized the possibility of a catalyst influencing the course of decomposition of organic substances, as may be seen from the data concerning decomposition of isoamyl alcohol of fermentation. Caventon [3] decomposed isoamyl alcohol by conducting it through a porcelain tube heated to redness. He reported only the composition of the gases formed, but from this one is unable to judge how the decomposition proceeded.

Thiele [4] decomposed isoamyl alcohol to obtain 1–3 butadiene. For safety in his experiments he employed an iron tube, but attached no significance to the possibility of the influence of iron upon the course of decomposition of the alcohol. Neither Caventon, Thiele, nor other writers paid attention to the liquid products formed during the pyrolysis.

In my first preliminary article which appeared in March, 1901, in the Berichte der Deutschen Chemischen Gesellschaft, I showed definitely the influence of catalysis, since there was only a slight decomposition of alcohol at 700° in a glass tube and considerable decomposition to aldehyde in an iron tube. The first experiment showed iron to be a contact agent, and indicated the possibility of obtaining aldehydes from alcohols on a large scale by a method which might successfully replace the old one of oxidation of alcohols with chromic acid mixture:

$$RCH_2OH \rightarrow H_2 + RCHO$$

Experiments were carried out on the catalytic production of formaldehyde, acetaldehyde, isobutyl and isoamyl aldehydes. Of course, in the first experiments the temperature was not measured very accurately, but it was approximately 560–600–700°. In the same study it was shown that secondary alcohols under the same conditions in the presence of the iron catalyst decompose into ketones and hydrogen. Methylisobutyl carbinol, which was synthesized in the laboratory, decomposed in the presence of iron to give methylisobutyl ketone.

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[1] Ann. Chim. Phys., *21*, 58 (1797); Ann. Phys., *2*, 208 (1799).

[2] Gmelin, Handbuch org. Chem., Vierte Auflage, 1848, IV, p. 551.

[3] Caventon, Ann., *127*, 93 (1863).

[4] Thiele, Ann., *308*, 330 (1899).

$$RCHOHR_1 \rightarrow H_2 + RCOR_1$$

Tertiary alcohols in the presence of the iron catalyst gave neither aldehydes nor ketones and thereby evidenced greater stability than the primary and secondary alcohols. For their pyrogenetic decomposition, a higher temperature was required, and various hydrocarbons (chiefly olefins), water, and insignificant amounts of carbon were obtained in the iron tube.

Therefore, my work in 1901 [1] for the first time established the exact picture of the decomposition of the three classes of alcohols at high temperature under the influence of an iron contact agent (catalyst) and gave an impetus to further investigations of pyrogenic reactions of organic compounds. These first investigations on the decomposition of alcohols show what part a catalyst may play at high temperatures in forcing a reaction to go in a definite direction. Further, I discovered in 1901 [2] that metallic zinc and its alloy with copper are the best catalysts for the aldehyde decomposition of alcohols, this alloy (brass) being now used in commercial plants. Later, other workers started to study the catalytic decomposition of alcohols, namely Knoevenagel [3] and Sabatier and Senderens.[4] Thus for example in 1902 I showed that copper oxide is a catalyst in the decomposition of alcohols. Sabatier and Senderens used reduced copper for the same purpose (1903), but this catalyst (as my experiments showed) soon became poisoned and necessitated an increase in the operating temperature.

The articles based on my studies which appeared in the Berichte der Deutschen Chemischen Gesellschaft doubtless facilitated considerably the work of other investigators and gave them new ideas leading to the testing of a whole series of catalysts, an undertaking impossible for one working alone in a laboratory.

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[1] Ipatieff, Ber., *34*, 9596 (1901). *id.*, 3579 (1901).

[3] Knoevenagel, Ber., *36*, 2816 (1903).

[4] Sabatier and Senderens, Compt. rend., *136*, 738 (1903).

DECOMPOSITION OF ETHYL ALCOHOL

In my study[1] "On Pyrogenetic Contact Reactions of Organic Compounds" these reactions were divided into two kinds: (1) Pyrogenetic reactions, which proceed under the influence of heat only, e.g., those in which the wall of the vessel does not influence the decomposition; (2) Catalytic (contact) pyrogenetic reactions, which occur in the presence of foreign substances, catalysts, which sometimes decrease very considerably the temperature of decomposition and thus cause marked increase in the yield of the chief product of the reaction. Of course, it is very difficult to estimate the influence of the walls of the vessel in which the reaction proceeds at high temperature, but such an opinion can be formed on the basis of the yield of the chief product and the course of the reaction.

My study of catalytic reactions started with the decomposition of alcohols. The procedure was as follows: Vapor from alcohol heated in a flask was passed through a tube containing a catalyst heated in a specially constructed gas or electric furnace. From the tube the decomposition products of the alcohol entered a large flask cooled with water and provided with a reflux condenser. From here the products passed through a spiral into a receiver cooled with a mixture of snow and salt. Gas passed from the receiver through two wash bottles before being collected in a gasometer for analysis. At the beginning of the experiment, air was displaced from the flask containing the alcohol and catalyst tube by means of carbon dioxide. The temperature of the catalyst tube was determined either by means of a le Chatelier pyrometer or by a thermometer.

Decomposition of Ethyl Alcohol in Glass

When ethyl alcohol was passed through a glass tube at 700° the alcohol distilled almost without decomposition. Insignificant amounts of gases were liberated, and traces of aldehyde were formed.

At about 750°, decomposition of ethyl alcohol became apparent by the liberation of gas and the formation of aldehyde. At a temperature of 800–820° an energetic decomposition of alcohol occurred. The amount of alcohol decomposed, of course, depended on the time of contact in the heated part of the tube. In order to make the experiments comparable, the vapor velocity was so fixed that equal quantities of alcohol were passed through the tube per unit time.

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[1] Ipatieff, Ber., *34*, 3579 (1901).

When 140 g. of ethanol was passed through the tube at 800–820°, 50 grams decomposed. Much of the material decomposed was converted into hydrogen and acetaldehyde. The latter at the high temperature decomposed further into more simple gases. A small part of the alcohol dehydrated into ethylene and water.

The quantity of aldehyde obtained in the reaction was determined in the form of aldehyde-ammonia. For this purpose the alcohol decomposition products boiling below 70° were diluted with ether and saturated with ammonia. From the weight of the crystalline aldehyde-ammonia obtained, the yield of aldehyde was calculated. Also the increase in weight of the gas wash bottles connected after the receivers was considered to be due to aldehyde since preliminary experiments showed that the aldehyde which did not have time to condense in the receivers was captured by these wash bottles. In all, nine grams of aldehyde was obtained.

Analysis of the gases by the method of Hempel gave the following results: ethylene, 11.5%; carbon monoxide 18.9%; methane 26.2%; and hydrogen 41.3%. After the removal of ethylene the gases contained 21.8% carbon monoxide, 41.6% hydrogen, and 30.3% methane.

In order to determine how much ethylene was formed by the decomposition of alcohol, an experiment was carried out at 820–830° on 140 g. of alcohol, 59 g. of which decomposed. The gas obtained by the decomposition was passed through a flask containing bromine. After removing the excess bromine, 45 g. of ethylene bromide was obtained, most of which boiled at 130–132° and solidified in ice to a crystalline mass.

If it is assumed [1] that all of the ethylene obtained originated from the decomposition of alcohol into ethylene and water,

$$C_2H_5OH \rightarrow C_2H_4 + H_2O$$

then the calculation shows that about 12 g. of alcohol should have been decomposed in the manner indicated by the above equation.

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[1] A small amount of ethylene might be obtained from the decomposition of acetaldehyde as we shall see later.

The other 47 g. of alcohol might have undergone decomposition according to another reaction,

$$C_2H_5OH \rightarrow H_2 + CH_3CHO$$

to give about 2 g. of hydrogen and 45 g. of aldehyde. In these experiments it was possible to obtain only about 17 g. of aldehyde, the remaining 28 g. of aldehyde decomposing at this temperature chiefly into carbon monoxide and methane.

$$CH_3CHO \rightarrow CO + CH_4$$

Such a reaction would give 10 g. of methane and 18 g. of carbon monoxide.

The above weights of these gases correspond to the following volumes under standard conditions: hydrogen, 22.32 l.; carbon monoxide, 14 l.; and methane, 15 l. A mixture of these three gases in the above proportions would have the following composition:

Analysis. Calculated: H_2, 43%; CH_4, 30%; CO, 27%. Found: H_2, 41.6%; CH_4, 31.4%; CO, 24.5%.

It is seen that the composition of the gas mixture calculated on the basis of an assumed course of decomposition approached quite closely the analysis of the gaseous mixture obtained. Such agreement justifies the equations given above. At the temperature studied, about one-fifth of the alcohol decomposed into ethylene and water and about four-fifths into hydrogen and aldehyde.

At this temperature [1] about one-third of the aldehyde formed originally did not have sufficient time to decompose, but the remaining two-thirds split into carbon monoxide and methane. The higher the temperature of decomposition of the alcohol, the more aldehyde formed, but also because of the temperature a greater amount of the latter decomposed. Therefore, at high temperatures an equalization of volumes is observed in the gaseous mixture of hydrogen, carbon monoxide, and methane. On the contrary, the lower the temperature of the decomposition of the alcohol, the larger the amount of aldehyde remaining, and the greater the proportion of hydrogen present in the gaseous mixture. Thus, the approximate course of the pyrogenetic decomposition of alcohol may be judged from the composition of the gas formed. Further experiments proved that assumption in the case of the decomposition of ethyl alcohol.

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[1] Of course, side reactions which lead to the formation of other products may occur here. But the latter are obtained in very small amounts and, therefore, we shall not discuss them. Thus, for example, the formation of insignificant amounts of formaldehyde and acetylene was observed.

In the literature, only a few examples were known of the formation of aldehyde by passing ethers through glowing tubes. The first experiment in this direction was described by Liebig [1] who obtained aldehyde from ether. Cannizzaro [2] by heating benzyl ether produced benzaldehyde and toluene. Tischenko [3] also obtained aldehydes from certain ethers (dimethyl and methyl propyl), but he did not state the amount of aldehyde and ethylene hydrocarbons formed. At present it is impossible to draw conclusions on the course of decomposition of ether on the basis of these data recorded in the literature. The gas analyses of Tischenko indicate, however, that the amount of hydrogen formed from ethers was considerably less than is the case in the decomposition of alcohol.

It is scarcely possible to explain the formation of aldehyde from alcohol by assuming the intermediate formation of ether which subsequently decomposes into methane and aldehyde.

$$C_2H_5OC_2H_5 \rightarrow CH_4 + CH_3CHO$$

It is much more plausible to explain the formation of aldehyde from ether in the following way: First, ether decomposes into ethylene and water (ethylene is present in the gas), and the water formed decomposes other molecules of ether forming molecules of alcohol; the latter by decomposition gives aldehyde and hydrogen. Up to this time, the decomposition of simple ethers under the influence of various catalysts (and in the absence) had not been a subject of a quantitative investigation, although it has considerable interest.

Thus, in 1901 when I first carried out the experiments on the pyrogenetic decomposition of ethanol at temperatures above 700° in a difficultly fusible glass tube, it became evident that ethyl alcohol may undergo two sorts of decompositions: (1) into aldehyde and hydrogen and (2) into ethylene and water, with no trace of carbon formation in the tube in spite of the high temperature. The last fact is very important because, if carbon were formed, one could not speak about two kinds of decomposition of alcohol under the sole influence of heat as carbon separated at the beginning might possibly become a catalyst later on and change the course of the decomposition of the alcohol.

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[1] Liebig, Ann., *14*, 134 (1835).

[2] Cannizzaro, Ann., *92*, 116 (1854).

[3] The action of the amalgamated aluminum upon alcohols. Dissertation.

Two years later, i.e., in 1903, after the influence of a catalyst and the possibility of catalytic decomposition in several ways had been shown by me, Knoevenagel[1] studied the decomposition of certain aromatic compounds. It is necessary to note that he worked at comparatively low temperatures, 200–230°, with aromatic compounds which were not very stable, but easily isomerizable and, therefore, his interesting conclusions cannot be readily compared with my investigations of catalytic decomposition at high temperature. Nevertheless, the results of Knoevenagel checked mine inasmuch as he showed that the decomposition of secondary aromatic alcohols produces ketones and that alcohols may give also simple ethers.

Decomposition of Ethanol in a Platinum Tube

The character of the pyrogenetic decomposition of ethanol in a platinum tube is the same as in a glass tube. However, this change occurs at a lower temperature in platinum than in glass. In the following experiments, ethanol was passed through a platinum tube which was heated directly by a gas flame over 80 cm. of its length. Of the 100 g. of alcohol passed through the tube at 660°, 70 grams decomposed. Of this quantity, 10 g. decomposed into ethylene and water and the remaining 60 g. into aldehyde and hydrogen. About 5 g. of aldehyde was absorbed by ammonia, and the remaining 55 g. of aldehyde decomposed into carbon monoxide and methane.

Calculations from the above results show that the gaseous products should have had the following composition:

Calculated, %	Observed, %
H_2, 34.2	H_2, 36.4
CO, 32.9	CO, 31.7
CH_4, 32.8	CH_4, 32.3

Thus, the actual analytical data coincide quite well with the calculated data. This agreement might serve as a proof for the given explanation of the pyrogenetic decomposition of ethanol.

In another experiment the platinum tube was supported by an iron trough in the gas furnace. From 145 g. of ethanol, 52 g. decomposed at 600–610°. Of this amount about 8 g. decomposed into ethylene and water, and the remaining 44 g. into aldehyde and hydrogen; 6 g. of aldehyde was absorbed by ammonia, and the remaining amount decomposed. The gas analysis gave the following results:

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[1] Knoevenagel, Ber., *36*, 2816 (1903).

$$H_2,\ 39.1\%;\ CO,\ 27.6\%;\ CH_4,\ 33.3\%$$

It is obvious that the course of this decomposition was similar to that of the preceding experiment.

To avoid overheating of the platinum tube, it was placed inside a wide iron tube which was heated to a strong red glow (up to 780°). From 117 g. of ethanol, 87 g. decomposed. Ten grams of acetaldehyde was absorbed by ammonia. Analysis of the gaseous products gave the following results:

Found, %	Calculated on Ethylene-Free Basis, %
C_2H_4, 10.8	H_2, 47.5
H_2, 42.5	CO, 20.8
CO, 18.6	CH_4, 31.6
CH_4, 28.3	

In the above case the formation of aldehyde and hydrogen was about twice as great as in previous experiments.

By calculating according to the analysis of the gases and the yields of the various products, the decomposition of ethanol in a platinum tube will be: About one-seventh of the alcohol decomposes according to the equation:

$$C_2H_5OH \rightarrow C_2H_4 + H_2O$$

and about six-sevenths according to the equation:

$$C_2H_5OH \rightarrow CH_3CHO + H_2$$

The higher the temperature of decomposition, the nearer the approach to equality observed in the resulting volumes of hydrogen, carbon monoxide, and methane. Of course, here as well as in the case of a glass tube, certain side reactions were observed; for example, the formation of a small amount of formaldehyde.

It was found that the decomposition of alcohol in a platinum tube starts at about 540°. One hundred grams of ethanol passed through a platinum tube at 600° during one hour. Twenty-three grams of alcohol decomposed, 17 g. of this being split into hydrogen and aldehyde; three grams of aldehyde was absorbed by ammonia and the remaining 14 g. of aldehyde decomposed into carbon monoxide and methane. Twenty-four liters of gas was obtained with the analysis:

$$C_nH_{2n},\ 1.4\%;\ CO,\ 24.5\%;\ H_2,\ 60.1\%;\ CH_4,\ 13.7\%$$

An insignificant amount of carbon was always obtained in the platinum tube.

Without doubt these experiments indicate that platinum is a catalyst in the decomposition of ethyl alcohol, because under the same temperature conditions the decomposition is three times greater in platinum than in glass.

Decomposition of Ethanol in a Porcelain Tube

Maintaining the conditions of the previous experiment, ethanol was passed with a velocity of 140–150 g. per hour through a porcelain tube at 750–780°. The decomposition proceeded in the same way as in the glass tube with 15 g. of alcohol decomposed; 7 g. of aldehyde and 12 g. of ethylene bromide were obtained. The analysis of the gaseous products gave the following results:

$$CO,\ 14.6\%;\ CH_4,\ 27.3\%;\ H_2,\ 58.8\%$$

Decomposition of Ethanol in a Copper Tube

Passing 140 g. of ethanol through a tube made of pure red copper, 46 g. of alcohol decomposed at 780–800°; 12 g. of aldehyde was absorbed by ammonia and 10 g. of ethylene bromide collected. The gas analyzed:

$$CO,\ 19\%;\ CH_4,\ 32.2\%;\ H_2,\ 49.5\%$$

It is evident from the above data that pure red copper is not a catalyst for the decomposition of alcohols.

Decomposition of Ethanol in an Aluminum Tube

No decomposition occurred when vapors of either absolute or 96% alcohol were passed through an aluminum tube placed in an iron tube and heated to 600°. Powdered aluminum, as we shall see later, produces a special kind of decomposition of alcohols.

DECOMPOSITION OF ALCOHOLS IN THE PRESENCE OF IRON CATALYST

The preliminary experiments on the decomposition of alcohols at high temperatures indicated the enormous influence of this catalyst upon the course of pyrolysis. Iron was the first catalyst which I discovered for dehydrogenation of alcohols and I showed soon afterward that it is also a hydrogenating catalyst.

If vapors of a primary alcohol are passed through an iron tube, or through a tube of difficultly fusible glass containing iron filings, an energetic decomposition of alcohols into aldehyde and hydrogen occurs when a temperature of 460 to 480° is reached:

$$RCH_2OH \rightarrow H_2 + RCHO$$

Vapors of a secondary alcohol decompose into ketone and hydrogen:

$$RCHOHR_1 \rightarrow H_2 + RCOR_1$$

Increase in the temperature of this catalytic reaction, of course, increases its velocity, and at a certain temperature the aldehyde starts to decompose into saturated hydrocarbons and carbon monoxide. Experiments showed that a part of the aldehyde may decompose to give small amounts of olefins (probably a decomposition of a saturated hydrocarbon into olefins and hydrogen occurs), and besides this in the presence of catalytic iron considerable carbon monoxide is reduced to methane. Further, depending upon the temperature of the reactions on the surface of the iron, a larger or smaller amount of carbon is formed.

The lower the temperature of decomposition of alcohol in the presence of catalytic iron, the more regularly proceeds the aldehyde or ketone decomposition of alcohol, with liberation of a gas consisting chiefly of hydrogen.

The following experiments on the aldehyde and ketone decomposition of alcohols present data for the above conclusions.

Ethanol

By leading 192 g. of alcohol through an iron tube in one hour at 700°, 144 g. decomposed; 20 g. of aldehyde and 27 g. of carbon were obtained. The gas analyzed:

$$C_2H_4, 0.8\%; CO, 21.1\%; CH_4, 12.1\%; H_4, 65.9\%$$

When 195 g. of alcohol was passed through the tube in one hour at 500°, only 23 g. of alcohol decomposed; 12 g. of aldehyde and 3 g. of carbon were obtained. The gas analysis was:

$$C_2H_4, 3.3\%; CO, 10.9\%; CH_4, 10.9\%; H_2, 71.9\%$$

For the experiment ordinary iron gas pipes were employed, the inside surface of which was rough and in spite of careful cleaning could not be made smooth. Other experiments made at 600° in steel tubes with highly polished inside surface gave exactly the same results as obtained in the rough iron pipes. Analysis of the gases gave:

$$C_2H_4,\ 1.3\%;\ CO,\ 19.1\%;\ CH_4,\ 8\%;\ H_2,\ 71.9\%$$

It was found that carbon formed by the decomposition of alcohol in iron and steel tubes contained particles of iron. To solve the question whether such carbon will produce a catalytic decomposition of alcohol, the following experiment was carried out: Six grams of carbon, obtained by decomposition of ethanol in a polished iron tube, was placed in a glass tube and 136 g. of alcohol was passed through the tube at 600°; 17 g. of aldehyde and 9 g. of ethylene bromide were obtained, and the carbon gained 4.5 grams in weight. The composition of gas was as follows:

$$CO,\ 17.4\%;\ CH_4,\ 8.3\%;\ H_2,\ 74.4\% \qquad \text{(without ethylene)}$$

The data show that under these conditions the same catalytic decomposition of alcohol takes place as was observed in an iron tube.

In order to decide the question as to which is the catalyst in the decomposition of alcohol, iron or carbon, the decomposition of alcohol was studied by passing it through a glass tube containing carbon which was free from iron. At 700°, from 134 g. of alcohol 17 g. was decomposed and 4 g. of aldehyde obtained. The carbon did not increase in weight. The composition of the gas was as follows:

$$C_nH_{2n},\ 3.6\%;\ CO,\ 23.2\%;\ CH_4,\ 22.3\%;\ H_2,\ 49.8\%$$

These experiments show that iron is an energetic catalyst for alcohol decomposition and it also appears to be the cause of the separation of carbon during decomposition of alcohol.

The following experiment was carried out to determine if carbon separation in the presence of iron was due to decomposition of alcohol or aldehyde. From 131 g. of paraldehyde passed through an iron tube at 600°, 120 g. was decomposed and 17 g. of carbon obtained. The composition of the gases was as follows:

$$C_2H_4,\ 3\%;\ CO,\ 42.6\%;\ CH_4,\ 38.5\%;\ H_2,\ 17\%$$

Thus, the chief product of decomposition of acetaldehyde in the presence of catalytic iron is methane and carbon monoxide.

$$CH_3CHO \rightarrow CH_4 + CO$$

There was considerable separation of carbon and it may therefore be assumed as highly probable that carbon is obtained because of the decomposition of aldehyde in the presence of catalytic iron.

Methyl Alcohol

Methyl alcohol is distinguished by its great stability at high temperatures. Experiments on pyrogenetic decomposition of methyl alcohol show that its stability approaches that of water.

Glass Tube.—Of 143 g. of methanol led through a glass tube heated up to 880° (the tube became fused), only 4 g. of alcohol decomposed and 1 g. of formaldehyde was obtained. The composition of the gas was the following:

$$CO,\ 16.1\%;\ CH_4,\ 5.4\%;\ H_2,\ 76.8\%$$

Porcelain Tube.—When 144 g. of alcohol was passed through a porcelain tube at 900°, 14 g. of alcohol decomposed and 4 g. of formaldehyde was obtained. Carbon did not separate.

The composition of the gas was:

$$CO,\ 24.1\%;\ CH_4,\ 2.3\%;\ H_2,\ 72.9\%$$

Iron Tube.—If the vapors of methanol are passed through an iron tube, the course of decomposition changes sharply. Iron is a very active catalyst for the decomposition of methanol and at 600° a very energetic decomposition of the alcohol proceeds with an enormous formation of gas.

When 200 g. of methyl alcohol was passed through the iron tube within one hour, almost all of it decomposed; small amounts of water and formaldehyde, 16 g. of carbon, and an enormous volume of gas were obtained. The composition of this gas was:

$$CO,\ 24.6\%;\ CH_4,\ 4.5\%;\ H_2,\ 70\%$$

Methyl alcohol decomposes into hydrogen and formaldehyde, and the latter under the influence of the iron catalyst decomposes into carbon monoxide and hydrogen. Olefin hydrocarbons were not found.

Isobutyl Alcohol

Almost no decomposition occurred when this alcohol was passed through a glass tube heated to 700°. But when it was led through an iron tube, rapid decomposition into isobutyric aldehyde and hydrogen occurred. This decomposition began at 450° and proceeded nicely at 480–500°.

In one experiment 190 g. of isobutyl alcohol passed through the iron tube in two hours at 470–480°, yielding 53 liters of gas and 70 g. of aldehyde. The composition of the gas was as follows:

$$C_nH_{2n},\ 5.4\%;\ CO,\ 4.2\%;\ CH_4,\ 4.3\%;\ H_2,\ 86.4\%$$

In another experiment 100 g. of isobutyl alcohol was led through an iron tube in one hour at 490–500°: 30 g. of aldehyde was obtained, and about 3 g. of carbon separated. The composition of the gas was:

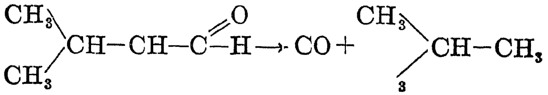
$$C_nH_{2n},\ 4.8\%;\ CO,\ 3.6\%;\ CH_2,\ 5\%;\ H_2,\ 86.6\%$$

Isoamyl Alcohol

Isoamyl alcohol of fermentation (b.p., 130–131°) also suffered almost no decomposition by passage through a glass tube heated to 700°, but in an iron tube energetic decomposition to aldehyde occurred. Thus in one hour 100 grams of isoamyl alcohol yielded 50 grams of aldehyde and a gas of the following composition:

$$C_nH_{2n},\ 11\%;\ CO_2,\ 1.2\%;\ CO,\ 9.4\%;\ C_nH_{2n+2},\ 13.6\%;\ H_2,\ 64.8\%$$

As will be discussed later, zinc and brass were superior to iron as catalysts for the large scale production of aldehydes from isobutyl and isoamyl alcohols. The difficulty with iron as catalyst was the formation of carbon in the tube and the appearance of a side reaction which produced olefin hydrocarbons as evidenced by the above gas analyses. The formation of these olefins may have been due to the decomposition of paraffins formed from aldehydes by loss of carbon monoxide. Thus isovaleric aldehyde formed catalytically from isoamyl alcohol might decompose into isobutane and carbon monoxide.



$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right> CH{-}CH{-}\overset{O}{C}{-}H \rightarrow CO + \left.\begin{matrix}CH_3\\{}_3\end{matrix}\right> CH{-}CH_3$$

This paraffin separating in the moment of its formation may undergo a further pyrolysis and as a result a series of olefins will be obtained.

For the determination of the character of these olefins, gases obtained by the decomposition of isoamyl alcohol in the iron tube were passed through two Drexel flasks containing bromine at 0°. A total of 1136 g. of bromide was obtained, which after several distillations gave the following fractions.

TABLE 1

Boiling Range of Fractions, °C.	Weight in Grams	Specific Gravity at 0°	Bromine Content in Per Cent	
			Found	Calculated for the Formula
1. 130–140°	150			
2. 140–143°	232	1.909	79.47	$C_3H_6Br_2$ = 79.2
3. 143–145°	152	1.909		
4. 145–147°	55	1.909		
5. 147–150°	99	1.966		
6. 150–155°	172	1.847		
7. 155–160°	70	1.818	72.52	$C_4H_8Br_2$ = 74.06
8. 160–165°	70	1.795	70.71	CHBr = 69.56
9. Above 165°	125	1.795	70.71	
Total	1085			

The investigation of all fractions made by Ogonovsky in our laboratory showed that the mixture of bromides consisted of the bromides of ethylene, propylene, the butylenes, and probably amylene. In the fractions boiling above 165° tribromides and butadiene tetrabromide ($C_4H_6Br_4$) were present.

In the early investigations of the pyrolysis of isoamyl alcohol in a porcelain tube at high temperature, Regnault and Wurtz determined the presence of ethylene, propylene, and butylene. Caventon [1] was the first to isolate butadiene from the gaseous decomposition products of isoamyl alcohol.

J. Thiele used the observation of Caventon for obtaining butadiene by decomposition of isoamyl alcohol using for this purpose an iron tube. He separated butadiene in the form of the tetrabromide, but did not study either the gases or liquids obtained by the pyrolysis. As will be discussed later, I had already shown in 1903 that butadiene may be prepared more conveniently from ethanol than from isoamyl alcohol.

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[1] Caventon, Ann., *127*, 95 (1863).

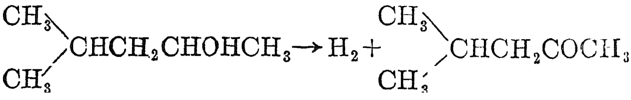
Secondary Alcohols

A slight decomposition occurred on leading vapors of isopropyl alcohol through a glass tube at 800°. Analysis of the products showed that the secondary alcohol decomposes also in two ways, (1) into acetone and hydrogen, and (2) into propylene and water. This is exactly the same picture of pyrolysis as was observed for ethanol in a glass tube.

Isopropyl alcohol and methyl isobutyl carbinol on passage through an iron tube at 600° decomposes chiefly into ketone and hydrogen:

$$\text{(I)}\quad CH_3CHOHCH_3 \rightarrow H_2 + CH_3COCH_3$$

(II)



$$\begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>CHCH_2CHOHCH_3 \rightarrow H_2 + \begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>CHCH_2COCH_3$$

Catalytic decomposition of a secondary alcohol in the presence of iron might be used with success for the production of ketones.

DECOMPOSITION OF ALCOHOLS IN THE PRESENCE OF A ZINC CATALYST

By leading vapors of various alcohols through an iron tube, it was observed that this decomposition proceeded at a lower temperature than in a glass tube and gave considerable quantities of aldehyde. It was interesting to study more closely why iron facilitates the decomposition of alcohol. If alcohol be considered as derived from water by replacement of one atom of hydrogen by an organic radical, then similar to water alcohol must decompose at a high temperature. Water, as is known, decomposes at 1000°; but in the presence of metals, as for example iron, it will decompose at a considerably lower temperature, namely at 640–660°, as shown by my experiments. Ethanol in a glass tube decomposes at 800°, but in an iron tube the splitting begins at 600–650°. In comparing the decompositions of water and alcohol in the presence of various metals we have to make an essential distinction. The decomposition of water by means of metals at high temperature is restricted to a limit because a non-reducible metal oxide is formed. The decomposition of alcohols in the presence of the same metals is not a limited reaction, since the metal taking part in the reaction remains unchanged, regardless of the amount of alcohol passed through it. Therefore, we have to consider such a reaction as a catalytic one. In order to determine which metals produce the catalytic decomposition of alcohols a whole series of experiments was made with other metals, namely: magnesium, aluminum, cadmium, tin, copper, lead, bismuth, antimony, manganese, nickel, and zinc. It was found that at a temperature of about 600° the vapors of alcohols do not suffer any change by coming in contact with copper, aluminum, lead, tin, bismuth, antimony, and magnesium; but by passing through manganese and nickel a decomposition occurs similar to that observed with the iron catalyst. Metallic zinc was found to be the best catalyst for decomposing alcohol into aldehyde and hydrogen. In this case the yields of aldehyde were larger than with the iron catalyst, because zinc was less active than iron in decomposing the newly formed aldehyde into saturated hydrocarbon and carbon monoxide. Also, only traces of carbon were formed. At certain places on the surface of the zinc an insignificant white layer of zinc oxide was observed.

If instead of metallic zinc, its alloy with copper in the form of brass was taken (filings of brass contained 33% of zinc and 67% of copper) then it was still found to be a catalyst for the aldehydic decomposition (about 600°). Very small amounts of zinc volatilized from the brass and precipitated on the cold part of the tube. During an experiment the brass increased in weight less than 1% and also, as in the case of zinc, became covered with a very slight coating of carbon and zinc oxide. As an example, I will mention an experiment on the decomposition of alcohol under the influence of zinc catalyst: 145 g. of ethanol was passed through a glass tube in which 137 g. of chemically pure zinc in sticks was placed and heated up to 620°. Thirty-five g. of alcohol was decomposed and 27 g. of aldehyde obtained which corresponded to a yield of 80% of the alcohol decomposed. Not more than one gram of ethylene was formed. The analysis of the gas gave:

$$H_2,\ 95.5\%;\ CO,\ 1.1\%;\ CH_4,\ 3.8\%$$

The experiment shows that zinc is an excellent catalyst for producing a large yield of aldehyde, because with this catalyst the product does not decompose further into carbon monoxide and methane.

It was interesting to compare the decomposition of ethanol with that of ethyl ether using the same zinc catalyst in order to show that the aldehyde forms directly by the decomposition of a molecule of alcohol without a primary formation of ethyl ether.

One hundred forty-five grams of ethyl ether was passed through a glass tube containing zinc. For the decomposition of ether a temperature above 700° was necessary. Under these conditions 35 g. of ether decomposed, and 10 g. of acetaldehyde and three grams of ethylene were obtained. The gas analysis gave the following results:

$$CO, 16.6\%; CH_4, 56.0\%; C_2H_6, 18.3\%; H_2, 11.7\%$$

Therefore, it is seen that the decomposition of ether is entirely different from that of alcohol and the temperature required for it is considerably higher.

In order to show the influence of degree of dispersion of the metal catalyst upon the course of decomposition of alcohols, it is interesting to mention an experiment that was carried out [1] on ethanol in the presence of zinc dust. The latter was purified and dried in a stream of an inert gas. By passing 134 g. of ethanol through a glass tube in which 100 g. of zinc dust was placed, 40 g. of alcohol was decomposed at 520–550°, and 10 g. of aldehyde and 76 g. of ethylene bromide were obtained. From these data it might be calculated that one-half of the alcohol decomposed into ethylene and water and only one-half split into aldehyde and hydrogen. The considerable decomposition of alcohol into ethylene and water might be explained, as will be discussed later, by the fact that oxides of certain metals produce an ethylene decomposition of alcohols. As zinc dust decomposes water at a low temperature (about 100–120°) the water formed in the first reaction should decompose with liberation of hydrogen and enrich the gaseous products with this element. Proof of such a decomposition is given by the gas analysis (after removal of ethylene):

$$CO, 4.3\%; CH_4, 5.7\%; H_2, 88.7\%$$

Experiments on decomposition of ethanol in the presence of zinc dust were done earlier by Jahn [2] who passed alcohol vapor over this material at 300–350° and another time at a dark red glow, probably about 600°. In the first case he obtained chiefly ethylene and water; in the latter at 600° the decomposition of alcohol in the presence of zinc dust proceeded in two directions: (1) into ethylene

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[1] Ipatieff, Ber., *34*, 3579, 3585 (1901).

[2] Jahn, Ber., *13*, 987 (1880).

TABLE 2

DECOMPOSITION OF ALCOHOLS IN THE PRESENCE OF THE ZINC CATALYST

SUBSTANCE	ALCOHOL, GRAMS	TIME OF REAC., MIN.	TEMP., °C.	CATALYST	ALDEHYDE, GRAMS	GAS, LITERS	GAS ANALYSIS IN %			
							C_nH_{2n}	CO	C_nH_{2n+2}	H_2
Ethyl Alcohol	145	60	620	Zn	27			1.1	3.8	95.5
" "	97	60	540	Zn	17	11	4.4	0.9	1.9	92.6
" "	100	70	560	Zn	40	19	1.2		3.0	95.2
" "	144	60	650	Brass	37			1.4	3.9	94.7
Isobutyl Alcohol	190	90	700	Zn	70			9.2	13.2	77.2
" "	146	60	680	Brass	67			10.1	12.0	79.0
" "	148	60	620	Brass	35			3.6	14.4	80.7
Isoamyl Alcohol	147	60	600	Brass	32			2.9	4.8	93.1
Benzyl Alcohol	112	30	680	Brass	35			26.4		74.1
Methyl Alcohol	143	60	620	Brass	4			0.5	2.0	97.2
Isopropyl Alcohol	88	45	620	Brass	$(CH_3)_2CO$ 30				2.0	98.0
Allyl Alcohol	82	35	600	Brass				48.8	15.0	36.7

and water, (2) into aldehyde and hydrogen. The content of carbon monoxide and methane in gases obtained in the experiments of Jahn might be explained by the decomposition of aldehyde formed in the first phase, but not by the direct decomposition of the ethanol molecule as Jahn thought. In Table 2, page 19, are summarized some of the many experiments carried out with zinc and brass as catalysts.

In certain of the experiments mentioned above, the percentage of ethylene hydrocarbons is not indicated, because the gases were passed through bromine and analyzed afterwards. The quantity of bromides obtained indicated that the formation of ethylene hydrocarbons was small. Besides this, it is necessary to note that ethylene hydrocarbons were obtained because of the decomposition of aldehydes formed.

Isobutyl Alcohol

As noted in the above table, zinc and brass are excellent catalysts for the aldehydic decomposition of isobutyl alcohol. The yield of aldehyde reached as high as 70% of the decomposition of the alcohol. It was noticed that after a long period of use brass became covered with a thin layer of carbon and lost its catalytic properties. Of course, at the present time it is easy to regenerate such a catalyst.

The unsaturated gaseous hydrocarbons obtained by this decomposition of isobutyl alcohol consisted chiefly of ethylene and propylene. The bottoms, from distilling the ethylene and propylene dibromides, solidified. The melting point was 76–78° after crystallizing from ethanol; the bromine content was determined as 66.4 and 66.1%. The structure of this product was not determined.

Allyl Alcohol

As an unsaturated alcohol, allyl alcohol with a boiling point of 95–96° was used for the experiments. By passage through brass filings 82 grams of allyl alcohol gave a considerable quantity of acrolein and a certain volume of unsaturated hydrocarbons which on bromination yielded 50 g. of a bromide. The distillation of the latter proved that the unsaturated hydrocarbons consisted chiefly of propylene and a small amount of divinyl.

The experiment showed that the decomposition of allyl alcohol proceeds similarly to that of the saturated alcohols, with the formation of an unsaturated aldehyde and hydrogen.

$$CH_2{=}CHCH_2OH \rightarrow H_2 + CH_2{=}CHCHO$$

However, the acrolein formed decomposed not into ethylene and carbon monoxide as expected by analogy with the saturated aldehydes, but into carbon monoxide, propylene, and probably divinyl. Of course, a polymerization of the acrolein formed was also possible here as well as splitting into the gases indicated above.

Benzyl Alcohol

In order to show that an aromatic alcohol will decompose the same as an aliphatic, benzyl alcohol was tried. A very slight decomposition of this alcohol (b.p., 201–206°) was noticed when 100 g. were passed through a copper tube heated up to 800°. Eight grams of aldehyde, 13 g. of benzene, and a small quantity of condensation products were obtained. The gas analysis gave the following results:

$$CO,\ 41.7\%;\ H_2,\ 58.3\%$$

The experiment showed that this decomposition proceeded in the same way as the catalytic splitting of the aliphatic alcohol.

$$C_6H_5CH_2OH \rightarrow H_2 + C_6H_5CHO$$

But at this high temperature a further decomposition into carbon monoxide and benzene occurred.

$$C_6H_5CHO \rightarrow C_6H_6 + CO$$

By passage of the aromatic alcohol through brass filings, decomposition was effected at a lower temperature and a good yield of aldehyde resulted as indicated in the table.

Methyl Alcohol

As indicated before, methyl alcohol decomposed energetically under the influence of an iron catalyst at a temperature as low as 600°. The gases formed had a composition closely approximating the theoretical for the decomposition of methyl alcohol, first into formaldehyde, and the latter into carbon monoxide and hydrogen.

$$CH_3OH \rightarrow CO + 2H_2$$

The theory requires:

$$CO, 33\%; H_2, 67\%$$

but the gas obtained contained:

$$CO, 24.6\%; CH_4, 4.5\%; H_2, 70.0\%$$

An entirely different picture is obtained, if methyl alcohol is passed through zinc or brass at 620°. The catalytic action of zinc upon methyl alcohol is weaker in comparison with its action on other alcohols, but what is very important to note is that here the aldehyde (formaldehyde) undergoes practically no decomposition as the gas analysis shows the presence of only traces of carbon monoxide:

$$CO, 0.6\%; CH_4, 2\%; H_2, 97.2\%$$

These comparisons of the actions of two catalysts as well as the demonstration of the possibility of a reversible reaction of hydrogenation of aldehydes into alcohols (as shown by my experiments under pressure [see a later chapter] and also by the experiments of Sabatier and Senderens) had without doubt [1] a significance in the discovery of the synthesis of methanol from carbon monoxide and hydrogen, as well as in the choice of zinc as catalyst, one that does not decompose formaldehyde, which can then be hydrogenated to methanol.

Isopropyl Alcohol

Almost a quantitative yield of acetone was obtained when isopropyl alcohol was passed through a glass or brass tube filled with brass filings and heated at 600–620°. The absence of carbon monoxide in the gaseous products was evidence of the stability of acetone at the temperature used.

From the beginning of my investigations in 1901, it was established that iron, nickel, manganese, zinc, and its alloys are catalysts for the aldehydic and ketonic decomposition of alcohols. Of these catalysts zinc and brass are best for preparation of aldehydes and ketones.

Tertiary alcohols behaved differently in the presence of the above catalysts as they required a higher temperature for decomposition than did primary and secondary alcohols.

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[1] Patart, Chemie et Industrie (1926).

In order to make it easier to follow the course of my investigations in catalysis, I will mention the theoretical considerations which laid the foundation for my later experiments, permitted creation of an hypothesis explaining the catalytic dehydrogenation of alcohols, and made it possible to predict new catalysts for this reaction. As stated previously, the difference in the decomposition of alcohol and water in the presence of a metal such as iron lies in the fact that the oxygen of the alcohol remains joined to the carbon atom and consequently the iron remains unchanged, while in the decomposition of water the oxygen combines with the metal forming an oxide. Therefore, the latter reaction is not catalytic. Since some metals decompose water easily and others with difficulty it was not to be expected that all metals would be able to decompose alcohols catalytically. Those metals which decompose water easily and consequently give readily reducible oxides might be catalysts for the aldehydic decomposition of alcohols. Experiments proved this assumption correct. On the other hand, metals such as tin, lead, copper, and others which would not decompose water were also not catalysts for the dehydrogenation of alcohol. But when the above oxides were reduced during reaction by the hydrogen liberated from the decomposition of the alcohol the resulting dispersed metals had catalytic activity.

Very small amounts of water may always be present in the decomposition of alcohols, either as moisture in the tube or in the alcohol, or in the form of hydroxide on the metal surface, or because of a slight dehydration of the alcohol into ethylene and water. This water on coming in contact with a metal able to decompose it, splits into hydrogen and oxygen, and the latter combines with the metal to form metal oxide. If this oxide reduces easily it will oxidize the alcohol into aldehyde with separation of water and regeneration of the metal. This cycle may be repeated indefinitely. Water will be decomposed by the metal giving hydrogen and metal oxide. Then the latter will again oxidize alcohol to aldehyde with formation of water and regeneration of the metal as indicated by the two equations:

$$C_2H_5OH + MeO \rightarrow H_2O + CH_3CHO + Me$$

("Me" stands for metal)

These equations show clearly that the quantity of metal will remain unchanged during the decomposition of all the alcohol into the aldehyde.

DEHYDROGENATION OF ALCOHOLS UNDER THE INFLUENCE OF METAL OXIDE CATALYSTS

In order to test the above explanation of the catalytic dehydrogenation of alcohols, I made a series of experiments on the decomposition of alcohols in the presence of metal oxides.[1] Reduction of the oxide by hydrogen would produce finely divided metal which might become covered with a layer of oxide and so act in turn as a strong catalyst for the decomposition of alcohol. Table 3 summarizes the results obtained with the following oxides: ferric, stannous, stannic, zinc, cupric, chromic, and nickelous.

From the results observed it follows that if a metal is a catalyst, its oxide also has catalytic activity although it might be incapable of complete reduction into finely dispersed metal. Thus, for example, zinc oxide is an excellent catalyst although it undergoes only slight reduction to the metal during use in the catalytic decomposition of alcohol. Here the formation of lower oxides of zinc is possibly the cause of the catalytic activity.[2] Perhaps a reciprocal reduction of zinc oxide and oxidation of the product occurs in amounts which we cannot observe just as the insignificant coating of zinc oxide forms upon zinc used in catalytic decomposition of alcohol. Here it is interesting to note that zinc used for dehydrogenation of alcohol above 430–450° first melts in the glass tube, and catalysis occurs on the surface of the molten metal, but as the catalysis proceeds at high temperatures (above 500°) the metal solidifies little by little. Perhaps this change may be explained by the presence of zinc oxide forming first on the metallic surface and later penetrating into the inner layers.

Proof that metal oxides take part in the catalytic dehydrogenation of alcohol in the presence of metals may be seen in experiments on the decomposition of alcohols in the presence of oxides of tin. No decomposition occurred when alcohol was passed over molten tin heated to 660–700° in a glass tube. However, if tin oxides were placed in the tube, energetic decomposition of alcohol took place at 650–660°. At the beginning of the reaction, the tin oxides

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[1] Ipatieff, Ber., *34*, 3589 (1901); Ber., *35*, 1047 (1902).

[2] For details see chapter on theory of catalysis.

TABLE 3

SUBSTANCE	ALCOHOL, G.	TIME, MIN.	T., °C.	CATALYST	ALDEHYDE OBTAINED, G.	GASES FORMED, L.	ANALYSIS OF GASES IN %				
							C_nH_{2n}	CO	C_nH_{2n+2}	H_2	CO_2
Ethyl Alcohol	145	60	660	ZnO	21						
" "	148	60	620	ZnO	18			3.8	3.9	91.5	
" "	140	60	600	Fe_2O_3	17			15.2	11.7	73.8	
" "	146	60	650	SnO_2	22			5.0	10.2	84.3	
" "	144	60	700	Sn red	17			15.3	22.0	63.4	
" "	146	60	600	CuO	15						
Isobutyl Alcohol	100	70	530	ZnO	38	21.5	1.8		3.2	91.8	3.2
" "	100	57	540	ZnO	25	22.0	0.8		3.5	94.5	1.2
" "	100	65	590	Cr_2O_3	2	15.0	11.6	3.0			1.8
" "	100	70	610	Cr_2O_3	2	24.0	20.0	13.0			1.2
" "	100	70	530	ZnO	30	27.0	4.4	2.4	14.5	78.0	1.0
" "	100	80	570	ZnO	44	29.0	4.0	1.2	12.6	81.4	0.8
" "	100	65	550	SnO	26	18.5	8.4		5.4	84.0	2.4
" "	100	60	620	SnO_2	40	14.0	12.8	3.2	12.1	65.5	6.4
" "	100	65	420	NiO	9	24.0	12.0	6.8	34.0	47.0	0.2
" "	100	70	450	NiO	16	23.5	11.4	2.0	29.9	56.0	0.2

were reduced by alcohols into finely dispersed metallic tin, which remained unmelted in spite of the high temperature within the tube. Six analyses of the finely dispersed, reduced tin obtained after the experiment showed 98.5% tin mixed with about 1% carbon. The fact that this finely dispersed tin did not melt induced the assumption that the surface of these small particles was covered with a very thin film of oxide. Such an oxide film participating in the reaction makes understandable the aldehydic decomposition of alcohol.

Exactly the same experiments were carried out with metallic copper and copper oxide. Red copper does not decompose water up to 800°. It is not a catalyst for decomposition of alcohol. On the other hand, copper oxide reduced by dehydrogenation of alcohols into finely dispersed copper containing copper oxides is a catalyst which was tested two years later by Sabatier and Senderens [1] when they employed reduced copper.

Thus, experiments carried out with metallic oxides and metals themselves [2] as well as observations made in studying the process, induced me to advance an hypothesis that water, hydrogen, and metal oxide participate in the catalytic dehydrogenation of alcohols. This hypothesis will be discussed in detail in the chapter On the Theory of Catalysis, but here, in order to strengthen the hypothesis, I shall mention a series of experiments [3] which I have made with other metals and their oxides.

Experiments with certain metals and oxides were carried out by me as early as 1902,[4] but because they were made with small quantities of materials, I considered it necessary to report later additional investigations in this direction and to present the conclusions which follow from all the experimental material obtained.

The experiments were carried out at ordinary pressure by passing vapors of isobutyl alcohol through a heated glass tube containing the metal oxide or metal. For comparison the following table includes data on decomposition in the presence of metals as well as of their oxides.

From the above results the following conclusions may be drawn:

(1) If a metal is a catalyst in the aldehydic decomposition of alcohol, then its oxide usually possesses the same property, even

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[1] Sabatier and Senderens, Compt. rend., *136*, 738 (1903).

[2] Ipatieff, Ber., *34*, 596, 3579 (1901).

[3] Ipatieff, J. Russ. Phys. Chem. Soc., *40*, 500 (1908).

[4] *Ibid.*, *34*, 182 (1902).

TABLE 4

Expt. No.	Catalyst	T., °C.	Time, Min.	Isobutyl Alcohol Charge, G.	Aldehyde Obtained, G.	Gas Formed, L.	Analysis of Gas in %				
							C_nH_{2n}	CO	C_nH_{2n+2}	H_2	CO_2
1	Cr	720	60	100	10	16.0	33.0	5.6	39.0	20.2	0.2
2	Cr_2O_3	600	65	100		13.0	11.8	3.2	21.7	62.0	1.6
3	Cr_2O_3	670	70	100		24.0	20.4	13.4	24.4	41.0	0.4
4	Mn	700	70	100	21	13.5	7.4		15.0	78.0	
5	Mn	710	65	100	22	15.0	12.2	1.4	15.1	71.4	
6	MnO_2	630	70	100	37	20.5	5.8		23.0	71.0	0.6
7	Fe	500	60	100	30	25.0	4.8	3.6	5.5	86.4	0.2
8	NiO	420	65	100	9	24.0	12.0	6.8	34.0	47.0	
9	Cu reduc.	520	60	100	41	16.0	1.2		1.0	97.5	0.2
10	Cu reduc.	570	60	100	31	12.0	2.8	1.0	3.0	93.0	0.2
11	Cu_2O	700	100	100	17	19.0	18.4	4.8	25.4	40.4	0.4
12	Zn	550	65	100	60	26.0	2.4		3.4	94.4	0.4
13	Zn	570	55	100	58	22.0	1.4		3.2	94.8	0.6
14	ZnO	530	70	100	30	27.0	4.4	2.4	14.5	78.0	1.0
15	ZnO	570	80	100	44	29.0	4.0	1.2	12.6	84.4	0.8
16	SnO	550	65	100	26	18.5	8.4		5.4	84.0	2.4
17	SnO_2	620	60	100	40	14.0	12.8	3.2	12.1	65.5	6.4
18	W	750	70	100	21	21.0	60.2		17.2	21.6	
19	UO_2	720	65	100	16	13.0	72.0		18.0	9.0	
20	Ag	670	75	60	8	8.0	22.6	5.4	30.2	39.7	
21	Ag_2O	700	60	72	5	8.5	25.2	7.2	30.0	35.2	

if incapable of complete reduction to finely dispersed metal. Thus, for example, zinc oxide which does not reduce into metallic zinc in marked amounts is an excellent catalyst.

(2) Observations of the catalytic action upon alcohols of metals and their oxides lead to the conclusion that this catalytic activity is related to the position of the element in the periodic system of Mendeléeff. If the metals are arranged in the order of increasing ability to produce the aldehydic decomposition of alcohols, the series follows: Chromium, manganese, iron, cobalt, nickel, copper, and zinc (see Expts. 1–16), which is the order of increasing atomic number.

It is evident that the catalytic activities of these metals follow their positions in the periodic table. Chromium causes only very slight aldehydic decomposition even at high temperatures, manganese and iron are very good catalysts, while cobalt and nickel cause very strong decomposition of alcohols to aldehydes. Reduced copper and metallic zinc are the best catalysts for the aldehydic decomposition of alcohols. While freshly reduced copper decomposes alcohol into hydrogen and aldehyde at 420–450°, this ability is soon lost and an increase of temperature up to 530–570° is required (see Expts. 9 and 10) in order that the reaction may continue. Contrary to the statement of Sabatier and Senderens, ethylene hydrocarbons are formed by the decomposition of alcohol in the presence of reduced copper.

(3) The ability to decompose the catalytically produced aldehyde into a saturated hydrocarbon and carbon monoxide increases in the series of catalysts manganese, iron, cobalt, and nickel with the ascending order of these metals in the periodic table. In spite of the high temperature, carbon monoxide was not formed in the presence of manganese, but with nickel the amount of carbon monoxide reached 6.8% (see Expt. 8) even with a lower temperature of reaction. Reduced copper and zinc caused almost no decomposition of the aldehyde to carbon monoxide.

Such a comparison of properties of catalysts with their action upon alcohols and a consideration of the conditions at which the catalytic reactions occur enabled us to understand many questions which at the beginning of the work appeared almost inexplicable. The comparison gave information on such questions as the temperature of decomposition, yield of aldehyde, and choice of catalyst.

Thus, for completeness of study of catalytic reactions of a definite type it is desirable to investigate the action of various catalysts in order to notice any relationship between the physical and chemical properties of catalysts and those transformations which take place under their influence.

(4) Metals and metal oxides with high atomic weights cause two sorts of decomposition of alcohols, namely, aldehydic and olefinic. The olefinic decomposition was especially noticeable with tungsten and uranium oxide (see Expts. 18 and 19); but the aldehydic decomposition was not observed with these catalysts.

(5) The best catalysts for producing aldehydes and ketones from alcohols are zinc and brass. Experiments showed (see Expts. 12 and 13) that when alcohol was passed through the same zinc two or three times its catalytic activity remained almost unchanged and the yields of aldehyde did not diminish. The activity of reduced copper (Expts. 9 and 10) weakens with use and it was never possible to obtain as large a yield of aldehyde with copper as with zinc. Besides this the reduced copper had to be prepared specially, but the zinc and brass for the aldehyde decomposition could be of any kind. Best practice consisted in filling brass tubes with brass filings. Sometimes it was useful to add to them 1–2% of zinc filings. At present, brass is the main catalyst used industrially for producing aldehydes and ketones from alcohols.

CATALYTIC DECOMPOSITION OF ALCOHOLS UNDER HIGH PRESSURE

From the beginning of my study on the catalytic dehydrogenation of alcohols at high temperatures (and at ordinary pressure) I was interested in the possibility of studying these reactions in a closed system from the viewpoint of chemical kinetics. I was also interested in determining whether these dehydrogenation catalysts could be used as catalysts for the hydrogenation of organic compounds—that is, whether they could catalyze the reaction in the reverse direction.

The dehydrogenation of alcohols and the hydrogenation of aromatic hydrocarbons were discovered simultaneously; the first by me, and the second by Sabatier and Senderens. From the beginning of this work, it could be supposed, with great probability, that these are reversible processes. But it was difficult at that time to answer the whole series of questions which arose concerning the reversibility of these catalytic reactions. The reduced nickel of Sabatier and Senderens had excellent properties for the hydrogenation of the aromatic nucleus, but at the same time it was found to be worse than iron as dehydrogenation catalyst [1] for producing aldehyde from alcohol. Therefore, it seemed necessary to study the equilibrium of catalytic reactions in a closed vessel, consequently under pressure. Pressure plays an important part in many chemical processes, causing reactions to occur which either do not take place at all or which proceed very slowly at ordinary pressure. On the contrary, high pressure may slow up some processes which take place readily at ordinary pressure. Ever since I discovered the catalytic dehydrogenation of alcohols I was anxious to study catalytic reactions under pressure. By introducing the influence of high pressure into the catalytic reactions of organic compounds, the activities of various catalysts could be determined and relationships developed which make possible the prediction of better catalysts.

Considering the fact that pressure decreases the speed of decomposition, it is conceivable that some reactions would reach a limit under certain pressures—that is they would be reversible.

Such assumptions, as will be seen from the succeeding discussion, were confirmed in part and the facts obtained were of value for the clarification of the course of catalytic processes studied by me under high, as well as at ordinary pressure.

Prior to my high pressure work, several reactions were known in organic chemistry (namely, plant practice for preparing dimethyl aniline and diphenyl amine) which necessarily had to be conducted under a pressure higher than atmospheric. But the pressures under which such reactions were usually conducted did not exceed 20–25 atmospheres. Besides this, as far as can be learned from the literature, the course of such reactions was not subjected to thorough study. Similarly, catalytic reactions of organic and inorganic compounds which were studied previously from various standpoints, were investigated only at ordinary pressure. Therefore, it was not known whether the characteristic activity of a catalyst at atmospheric pressure would be maintained completely or partially when the process caused by it occurred under high pressure.

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[1] Ipatieff, Ber., *34*, 596, 3579 (1901); *ibid.*, *35*, 1047 (1902).

The High Pressure Apparatus

Pressure was not introduced sooner into the study of catalytic reactions because of experimental difficulties involved. The chief difficulty consisted in the construction of an apparatus which could be heated to 600° while under several hundred atmospheres pressure. Also, the apparatus had to be constructed in such a way that the pressure developed within could be measured continuously throughout the experiment, and so that all the gaseous products of decomposition of the organic compounds could be discharged slowly at the end of the experiment.

After many trials, I finally succeeded in constructing a high pressure apparatus which enabled me to perform thousands of experiments. The temperature in this apparatus sometimes reached 600° and the pressure at this temperature was about 400 atmospheres. At low temperatures this apparatus could withstand pressures up to 1300 atmospheres. Such an apparatus (bomb) was first constructed according to my drawings in the private workshop of Malwistrem, a mechanical engineer, and later in the Longenzipen plant in St. Petersburg.

The apparatus made in the Longenzipen plant consisted of tube *A*, cover *B*, pressure gage *K*, and gasket *L* (Fig. 1a). The tube *A* was made of the best soft malleable steel and was tested under a pressure of 600 atmospheres while being heated up to 500°. Instead of such a tube, a Mannesmann's drawn tube could be used. Originally, the tubes had a capacity of 250–270 cc. with inside diameter of about 2.5 cm. Later, tubes of various capacities up to 3 liters were employed. To the open end of the tube was fitted a flange with three holes through which bolts could be inserted. The cover was equipped with a flange with three holes for bolts, and two short tubes, *c* and *d*. Tube *d* was connected to the pressure gage *K*. Tube *c* was closed by a valve through which gas could be discharged from the bomb, or charged into it by means of a pump. Tight closure between the mouth of the bomb and the cover was obtained by means of a copper gasket which consisted of a disc of red copper with a hole in the middle. The knife-edge around the open end of the tube and the knife-edge on the inside of the cover cut deeply into the copper gasket when the cover was clamped to the tube by means of the bolts. The drawing together by means of the

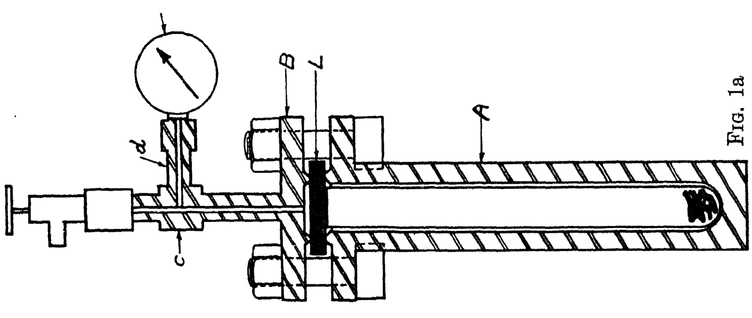

FIG. 1a

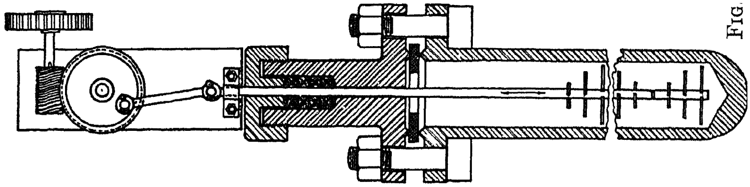

FIG.

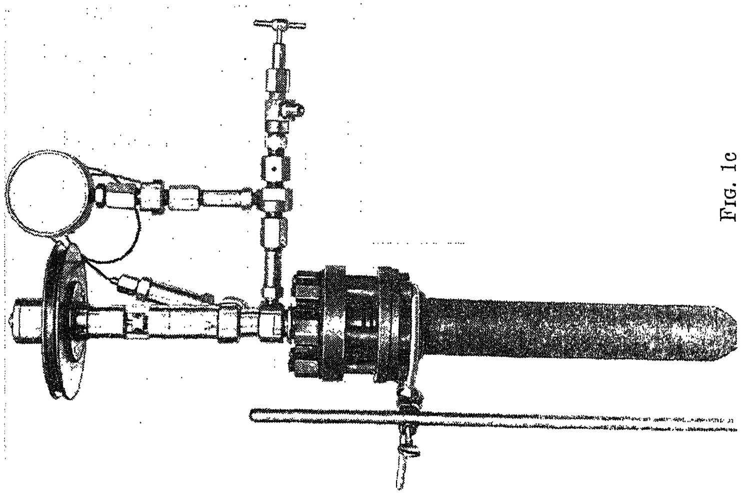

FIG. 1c

bolts had to be uniform, but strong. Usually the pressure gage was screwed to the cover for a long time. When it was desired to close the bomb, the valve was turned. The valve may have various arrangements, but usually it closed the apparatus by means of a cone pressed into a seat by means of a finely cut screw. (It was so arranged in the first model of the apparatus and except for a very slight change was similar to the valve construction on the calorimetric bomb of Sarro and Wielle). The valve must not be closed with too much force else it will be damaged. Provided the knife-edge of the tube came directly opposite the knife-edge of the cover and the copper gasket was placed every time in the same position, the closure was good for many experiments.

The steel tube of the bomb was also fitted with liners prepared from various metals, such as nickel, chrome-nickel steel, phosphor bronze, copper, silver, and also from glass for use in cases where these materials were not catalysts. In the apparatus made with copper walls, various catalysts might be introduced. The gaskets were made of other metals when copper could not be used. Very good gaskets were prepared from molten silver. Silver liners were placed in the apparatus and silver gaskets were used when I studied the oxidation of phosphorus by water under pressure in order to obtain phosphoric acid.

Method of Investigation

The bomb, containing the substance and the gas, was heated in an electric furnace which had a coil made of nickel wire and asbestos filling. The asbestos served not only for insulation, but it also decreased the danger of the apparatus being shattered into pieces in case of an explosion. The heating current, which did not exceed 10 amperes, was regulated by a resistance. The temperature was measured at intervals of 5 to 10° by a Le Chatelier pyrometer or a thermometer, which in the preliminary experiments, touched the heated apparatus. Later, the thermometer was introduced inside of the apparatus by means of a special tube or thermo-well.

In the bombs of 250–270 cc. capacity, 20–50 g. of the organic compound was used. If a special catalyst was not introduced, the walls of the bomb served as catalyst. After pouring in the liquid, the bomb was closed by its cover and the air was pumped out through a valve which was subsequently closed. The charged bomb was placed in the electric furnace which was heated at the maximum current strength (about 9 amperes) until the pyrometer indicated the temperature at which the experiment was to be performed. In certain experiments the charged bomb was placed in the furnace after the latter had been brought to the desired temperature, but introduction of this heavy apparatus caused a large drop in the temperature of the furnace. The course of heating under these conditions differed slightly from that of a bomb placed in a cold furnace. Recently, we began to use metallic baths (an alloy of lead and tin in equal parts is convenient). When these were used the temperature of the apparatus rose rapidly, reaching the desired value within three to four minutes, and it was very convenient to regulate the temperature of the process. At a certain temperature, the pressure gage began to indicate the vapor pressure of the organic substances within the bomb. From this moment, readings were taken of the temperature (T), time (t), and pressure (p).

All my experiments with alcohols were made at temperatures above the critical and consequently these substances were in the vapor state. Therefore, at the beginning of the experiment, the pressure indicated by the pressure gage represented only the pressure of alcohol vapors at various temperatures, but around 450°, at which temperature the decomposition of alcohol began, the pressure gage showed the sum of the vapor pressure of the alcohol which remained undecomposed plus the vapor pressure of the decomposition products. With increasing temperature the decomposition products were responsible for a greater and greater part of the total pressure. Experiment showed that all the alcohol decomposed at a temperature above 500°. If the increase of the pressure of the alcohol vapor heated above 450°, follows the law,

$$p = p_o(1 + \alpha t),$$

it is evident that if no decomposition of alcohol takes place, the increase in pressure will be proportional to the temperature (with a certain approximation) and for each temperature there will be a corresponding pressure which will not depend on the time of heating.

But if the alcohol undergoes decomposition, then this proportionality between pressures and temperatures will not hold. Experiments showed that the shape of the curve, expressing this relationship, will indicate the amount of decomposition occurring and the increase in pressure will depend upon the time of heating. At each temperature at which decomposition of an organic compound proceeds, the increase in pressure in a certain interval of time (dp/dt) might be considered, with sufficient accuracy, as a value proportional to the velocity of decomposition of the substance. If a catalyst is introduced under a given set of conditions, and comparison is made of the increase in pressure in the presence and absence of the catalyst, an idea can be gained concerning the accelerating action produced upon the decomposition by the catalyst. Thus, we may gain an idea as to the maximum and average velocity of decomposition of organic compounds at high temperatures and pressures.

In order to show the course of decomposition of organic compounds, curves were constructed expressing the relationship between the pressures developed by the decompositions and the times of the heating. Pressures in atmospheres, as shown by the pressure gage, were plotted as ordinates against time in minutes as abscissae. A study of the curves of pressure increase for various compounds led to the conclusion that the value most characteristic of the course of the decomposition of the given compound is not the average pressure increase during the decomposition, but the maximum velocity of pressure increase $(dp/dt)_{\text{max}}$. This value is proportional to the maximum velocity of the decomposition of organic compounds and it is geometrically the tangent of the largest angle formed by a tangent to the curve and the abscissa axis.

The maximum velocity of pressure increase is the most characteristic value of the reaction as it belongs to that period of the decomposition which is affected least by side reactions. Therefore, it can be calculated with sufficient accuracy. This value is interesting inasmuch as the product of this value, multiplied by the time necessary to bring about maximum pressure (p_{max}) is a constant for alcohols.

$$(dp/dt)_{\text{max}} \cdot t = K = \text{Constant}$$

This relationship shows that if the velocity of the decomposition of alcohol decreases, then the time required to reach the maximum pressure p_{max} will increase. This product is found to remain constant for a whole series of temperatures; the initial decomposition temperature varies somewhat for different alcohols. Besides this, the magnitude of the constant K changes for the different alcohols and it also depends upon the character of the catalyst. For iron, the constant K is almost twice as large as for alumina. As this constant K may serve as a measure of the decomposition of alcohols, the relationship of K_o, K, and K_1 obtained with various catalysts,

$$K : K_1 = K_o,$$

may serve for the approximate comparison of the action of various catalysts upon the same substance at a given temperature. All these generalizations may be only rough approximations of the reality, but they are based on the experimental material reported below. Also they served as the leading motive in my study of the course of decomposition under high pressure. The decomposition of alcohols under pressure in the presence of metals will be discussed first.

PRIMARY ALCOHOLS

As shown by my previous experiments, primary alcohols decompose into aldehyde and hydrogen in the presence of iron and zinc catalysts. If the temperature is high the aldehyde decomposes further into a saturated hydrocarbon and carbon monoxide:

$$RCH_2OH \rightarrow H_2 + RCHO$$

$$RCHO \rightarrow RH + CO$$

The same reaction occurs when the alcohol is heated in a closed iron apparatus but a higher temperature is required to cause the aldehydic decomposition under high pressure than is necessary at ordinary pressure, i.e., pressure diminishes the catalytic action of the metal. The second circumstance distinguishing decomposition under pressure in the presence of a catalyst is the formation, in certain cases, of special products which were not liberated by decomposition at ordinary pressure. Furthermore, there is *no formation of carbon* in the decomposition of alcohol under pressure. Also, the gaseous products are predominantly saturated hydrocarbons (from two-thirds to three-fourths), sometimes mixed with a considerable amount of carbon dioxide.

Ethyl Alcohol

When ethyl alcohol was passed through a copper tube under ordinary pressure at 580° its decomposition was so slight that only traces of aldehyde were obtained. But, when the alcohol (40 g.) was heated in a high pressure apparatus with copper walls, slow decomposition occurred at 530°. After 285 minutes, a pressure of 180 atmospheres was reached; the value $(dp/dt)_{\max}$ was equal to about 1. After cooling the tube, the pressure was 24 atmospheres. A total of 3.9 liters of gas was released and 29 g. of liquid obtained. The analysis of the gases was as follows:

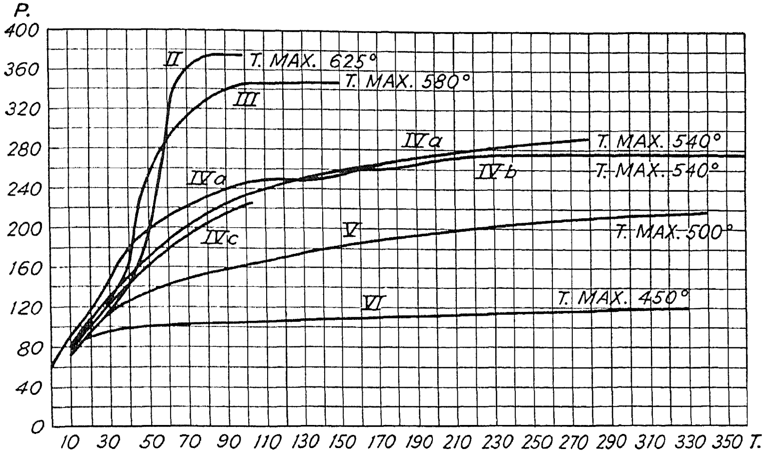

FIG. 2

CO_2, 3.6%; CO, 6%; O_2, 1.2%; C_nH_{2n}, 10.4%; C_nH_{2n+2}, 33.4%; H_2, 45.4%

The liquid contained traces of aldehyde and small amounts of water, the latter formed by the decomposition of ethyl alcohol into ethylene and water. These data show that copper is not a catalyst for the decomposition of alcohols under high pressure.

When ethyl alcohol was heated in an iron tube, energetic catalytic decomposition took place, the velocity of which depended upon the temperature. The curves of pressure increase for temperatures of 625°, 580°, 540°, 508°, and 450° are designated by numerals II, III, IV, V, and VI (Fig. 2). The same numerals also designate the corresponding tables which give the

TABLE 5

DECOMPOSITION OF 40 GRAMS ETHYL ALCOHOL UNDER PRESSURE IN AN IRON TUBE

Table II, Curve II			*Table III, Curve III*			*Table IV, Curve IV*			*Table V, Curve V*			*Table VI, Curve VI*		
TIME, MIN.	T., °C.	p, ATMS.	TIME, MIN.	T., °C.	p, ATMS.	TIME, MIN.	T., °C.	p, ATMS.	TIME, MIN.	T., °C.	p, ATMS.	TIME, MIN.	T., °C.	p, AMTS.
0	370	57	0	380	43	0	440	58	0	380	58	0	400	59
10	430	76	10	440	76	10	480	90	10	440	83	10	445	85
20	480	99	20	500	103	20	505	109	20	480	101	20	450	96
30	520	119	30	530	126	30	530	140	30	505	119	30	450	99
40	540	144	40	560	168	35	540	160	40	508	128	40	449	100
45	555	164	45	575	201	40	540	180	50	506	136	50	450	100
50	575	198	50	580	241	50	540	190	60	507	143	110	447	100
55	590	248	55	580	265	60	538	210	70	509	152	170	444	110
60	605	300	60	575	283	70	539	230	80	510	160	230	451	115
65	615	340	65	578	300	80	540	240	90	508	164	290	450	120
70	625	363	70	580	313	90	550	248	155	509	188	350	448	120
75	625	372	80	580	330	110	540	250	325	509	216			
80	625	373	90	580	340	130	540	258	335		218			
95	625	373	100	580	344	160	540	262						
100	625	373	150	580	344	180	540	262						
						200	540	268						
						420	540	272						

change of pressure, (p), with time, (t), in the decomposition of 40 g. of ethyl alcohol at the above-mentioned temperatures.

From the data presented in the tables, it is seen that in the decomposition of alcohol at 625°: the value of $(dp/dt)_{\max}$ is equal to $52/5 = 10.4$ kilos per minute; the time required to reach the maximum pressure was 75 minutes and the product $(dp/dt)_{\max} \cdot t = 780$ kilo minutes.

In the decomposition of alcohol at 580°: $(dp/dt)_{\max} = 40/5 = 8$ kilos per minute, and 100 minutes (t) was required to reach the maximum pressure of 344 atmospheres. Therefore, $(dp/dt)_{\max} \cdot t = 800$ k.m.

In the decomposition of alcohol at 540°: $(dp/dt)_{\max} = 20/5 = 4$ kilos per minute; a time of 200 minutes corresponded to the maximum pressure of 268 atmospheres and therefore $(dp/dt)_{\max} \cdot t = 800$ k.m.

In the decomposition of alcohol at 510°: $(dp/dt)_{\max} = 18/10 = 1.8$ kilos per minute; the product of this and the total time of 335 minutes is equal to 603 k.m., but the decomposition was not finished and there is reason to assume that it would have continued for another hour.

Curve IVb gives a $(dp/dt)_{\max}$ of 2.4 kilos per minute; the product $(dp/dt)_{\max} \cdot t = 720$ k.m.[1]

Curve IVc is constructed from the data of an experiment made for the purpose of determining the character of the gaseous products obtained by heating alcohol in the apparatus at 540° before maximum pressure was reached.

In order to be able better to judge the character of the decomposition of ethyl alcohol in the high pressure apparatus, the data obtained in a whole series of experiments have been collected and are summarized in Table 6.

In this table are listed two series of high pressure experiments and one series of experiments made at ordinary pressure. Results on the decomposition of ethyl alcohol at ordinary pressure are given here in order to compare them with the data obtained on the decomposition of this substance under high pressures. It is obvious that the decomposition of ethyl alcohol takes place at much lower temperatures and more rapidly at atmospheric pressure

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[1] This experiment was not quite complete. After 280 minutes $p_{\max}$ was not yet reached. It can be assumed that the equilibrium would be reached after ten to twenty more minutes.

TABLE 6

CATALYTIC DECOMPOSITION OF ETHYL ALCOHOL

EXPT. No.	CURVE No.	TIME, MIN.	T., °C.	CATALYST	PRESS., ATMS.		LIQUID RECOVERED, G.	GAS PRODUCED, L.	ANALYSIS OF GAS IN %					
					Max.	Final, after Cooling			C_nH_{2n}	CO_2	O_2+N_2	CO	H_2	C_nH_{2n+2}
323	I	180	530		180	24	27	3.90	10.4	3.6	1.2	6.0	45.4	33.4
326	II	100	625	Fe	373	89	3	25.50	7.8	6.2	1.4	6.2	12.2	66.2
328	III	150	580	Fe	344	88	3	25.10	8.0	7.6	1.0	4.0	13.0	67.0
331	IV	420	540	Fe	272	67	12	19.65	1.8	13.4	1.4	3.6	28.0	51.8
330	IVb	280	540	Fe	289	66	13	19.40			1.2	5.4	22.0	58.2
333	IVc	95	540	Fe	226	42	25	11.25	5.2	4.2	1.4	13.2	18.0	58.0
331	V	335	510	Fe	218	43	23	11.85	5.8	4.0	1.2	12.0	20.0	57.0
332	VI	350	450	Fe	120	8	34	2.05	10.4	1.2	1.6	4.8	43.6	37.8
246		99	510	Fe	High pressure			5.00	20.4	2.0	0.8	9.0	34.6	33.2
252		40	520	Fe				7.50	19.4	2.6	1.0	11.2	31.4	34.8
247		50	530	Fe				8.20	15.2	2.0	1.0	13.8	31.6	36.4
258		35	540	Fe				10.60	7.0	4.0	0.8	15.8	24.2	48.2
250		60	550	Fe				11.50	7.0	5.0	0.8	13.0	20.2	54.0
292		80	620	Fe				24.90	8.0	10.1	0.8	2.4	12.3	66.4
256		85	450	Fe	1		8 g. aldehyde	13.00	11.4	3.0	1.0	1.2	74.8	8.6
260		60	500	Fe	1		10 g. aldehyde	28.00	6.0	2.2	1.0	5.0		
253		45	625	Fe	1		1 g. carbon	28.00	4.6	3.0	0.6	16.2	65.4	10.2

than it does under higher pressure. Below 525° the decomposition is mainly aldehydic as evidenced by the abundance of hydrogen in the gaseous products; carbon begins to form on the walls of the tube at about 525°.

At high pressure the decomposition starts around 450° and proceeds very slowly to a certain limit (Curve VI) since the curve becomes parallel to the abscissa axis when the pressure reaches 118 atmospheres. According to the gas analysis, it is evident that besides the aldehydic decomposition, there is also a decomposition of the aldehyde itself which is accompanied by the formation of a large amount of saturated hydrocarbons, chiefly methane. This is quite different from the decomposition of ethyl alcohol at 450° under ordinary pressure. Starting at 510°, the decomposition of ethyl alcohol in the high pressure apparatus proceeds with greater speed than at 450° and the above-mentioned regularity is observed, namely, that the product of $(dp/dt)_{\max}$ and the time (t) required to attain maximum pressure approaches a constant, about 800 kilo minutes.

The curves, expressing the increase of pressure, consist of three branches. The first branch, ascending to approximately 120 atmospheres, represents chiefly the increase of the vapor tension of ethyl alcohol and these portions of the curves run parallel to each other in the various experiments. The second branch of the curve, which represents the increase of pressure due to the decomposition of the alcohol, is the most characteristic part of the curve and its shape will be different when we pass from one maximum temperature to another. The acceleration of the decomposition of alcohol is a value dependent upon the catalyst and upon the temperature. The third branch of curves of pressure increase starts where the curve becomes parallel to the abscissa axis, i.e., when a maximum pressure is reached in the alcohol decomposition and an equilibrium is established in the gaseous products of decomposition. On the other hand, such a branch of the curve may also indicate a certain limit reached by the decomposition reaction. But the existence of a limit of decomposition might be assumed only in the case where a reversible reaction exists between the decomposition products of alcohol, e.g., between aldehyde and hydrogen. Then the limit of the reaction would be a function of temperature and pressure. Experiments which will be discussed later show that the decomposition of alcohol into aldehyde and hydrogen in the presence of a catalyst such as iron, zinc, and others is actually a reversible reaction, but, in certain cases, it is complicated by the formation of new products not found at ordinary pressure.

Thus, in a closed apparatus under pressure the decomposition of alcohol proceeds more complexly because of side reactions caused by the development of high pressures. The pressure opposes the complete decomposition of organic compounds and increases the limit of those side reactions which may or may not take place, or which may escape our attention because of their insignificance, in the course of the process at ordinary pressure. But the experiments on decomposition of ethanol lead to the conclusion that there exists such a *critical temperature of decomposition* at which alcohol decomposes into the simplest gaseous compounds. Such a temperature for ethyl alcohol is in the neighborhood of 580°. The further heating of alcohol is superfluous because at 625° an equal volume of gas, about 25 liters, having a composition similar to that produced at 580°, is obtained, but, of course under conditions of an equal time of heating. The time of heating at a given temperature has a great influence upon the amount of decomposition products formed, as well as upon their composition. In Table 6 in the second series of experiments and also in Experiment 333 (Curve IV), the time of heating was short and the volume of gas obtained and its composition differed from the corresponding results obtained on long heating.

Concerning the composition of the gases, the experiments on the decomposition of alcohol under high pressures lead to the conclusion that with increase in pressure the gaseous products become richer in saturated hydrocarbons and poorer in hydrogen, and that the percentage of carbon monoxide first increases to a certain limit and then drops. This change in the gas composition, depending upon pressure and temperature, indicates that a catalytic reaction occurs between the gaseous products.

Sabatier and Senderens showed that carbon monoxide and carbon dioxide are easily reduced to methane at ordinary pressure in the presence of reduced nickel; other metals bring about this reduction to a much smaller extent. Iron might be a catalyst for the conversion of carbon monoxide into methane under high pressures as evidenced by the gas analyses obtained in the decomposition of ethanol. On the other hand, the *absence of the formation of carbon* [1] in the decomposition of alcohol in an iron bomb under high pressure indicates also that the carbon which might separate during the splitting of the alcohol meets hydrogen at the moment of liberation and forms methane due to the influence of pressure and catalysts. At ordinary pressure, the decomposition of ethanol in iron tubes above 520° proceeds with carbon deposition.

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[1] The decomposition of the most simple organic compounds under pressure in

In addition to acetaldehyde, the liquid products obtained by the decomposition of ethanol under pressure always contained a small amount of liquid, insoluble in water, which was unsaturated as shown by its ability to decolorize potassium permanganate and to add bromine. In order to determine the character of this product and the conditions of its formation, special experiments were made which will be described later.

As a result of all these investigations with ethyl alcohol, it follows that the catalyst iron acts more weakly under high pressures than at atmospheric pressure, and, while the fundamental reaction in the decomposition of alcohol into aldehyde and hydrogen remains the same, the course of the decomposition is strongly influenced by the factors of pressure and time of heating. The final products of the decomposition of alcohol under high pressure are distinctly different from the decomposition products of this substance at ordinary pressure. Because of the amount of saturated hydrocarbons formed, the decomposition of alcohol under pressure could be called *paraffinic*.

Propyl Alcohol

Normal propyl alcohol, the same quantity as ethyl alcohol (40 g.), was heated in the high pressure apparatus already described. Two experiments were made, Nos. 369 and 370. Tables IX and X below show the changes of temperature and pressure during the experiments (page 44).

An inspection of Curves IX and X shows that they have three branches which have the same significance as those obtained with ethyl alcohol. In the first curve the maximum velocity of pressure increase $(dp/dt)_{max}$ equals 8 kilos per minute and the product obtained by multiplying this value by the time in minutes required

the presence and in the absence of hydrogen, without the participation of special catalysts (only the iron walls of the bomb), and without formation of carbon, first carried out by me in 1904, without doubt led Bergius in 1911 to the idea of making experiments under pressure in the presence of hydrogen on the decomposition of more complex organic materials such as brown coal, petroleum residues, and tars. See articles of Kling, Chemie et Industrie, *11*, 1067–77, 1645 (1924).

TABLE 7

Table IX, Curve IX			*Table X, Curve X*		
Time, Min.	T., ° C.	Press., p, Atms.	Time, Min.	T., ° C.	Press., p, Atms.
0	380	21	0	385	28
10	410	41	10	430	50
20	450	52	20	475	62
30	490	62	30	505	73
40	515	71	40	535	89
50	540	80	50	560	120
60	565	92	60	585	190
70	585	123	65	600	240
75	572	152	70	610	284
80	598	192	80	620	310
85	605	232	90	620	310
95	615	290	100	620	310
100	618	301			
105	620	301			

to reach maximum pressure is equal to $(dp/dt)_{\max} \cdot 100 = 800$ kilo minutes. For the other curve $(dp/dt)_{\max}$ equals 10 kilos per minute and $(dp/dt)_{\max} \cdot 80 = 800$ k.m. The constant K for propyl alcohol is the same as for ethanol.

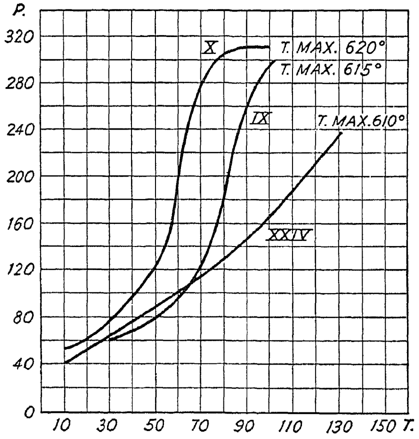


Fig. 3

The decomposition products of propyl alcohol at 620° consisted chiefly of gases; only three grams of liquid was recovered and this consisted of water and condensation products.

The composition of the gases is given in Table 8.

The gases contained much methane and ethane and a little carbon monoxide and hydrogen. These gaseous products were of the same composition as those from ethanol.

Isoamyl Alcohol

Isoamyl alcohol (boiling point, 129–130°) was heated under pressure in the presence of iron and of zinc. In the latter case, 31

TABLE 8

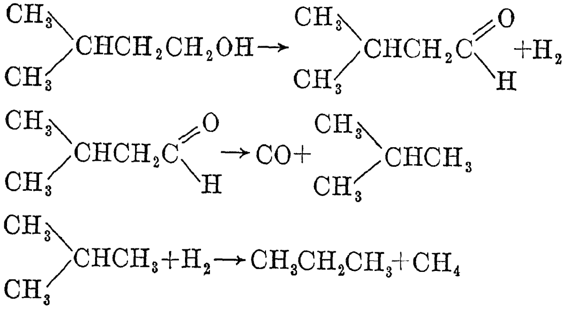
Expt. No.	Curve No.	Time, Min.	T., °C.	p_{max}, Atms.	p after Cooling, Atms.	Catalyst	Analysis of Gases in %						Liquid Products, G.
							C_nH_{2n}	CO_2	O_2	CO	H_2	C_nH_{2n+2}	
369	IX	100	615	301	68.0	Fe	2.4	13.0	1.0	6.0		77.8	3
370	X	100	620	310	69.5	Fe	2.4	13.6	1.0	3.8	7.4	71.6	2

TABLE 9

Table XII			*Table XIII*			*Table XIV*			*Table XV*			*Table XVI*			*Table XVII*			*Table XVIII*		
Time, Min.	T., °C.	p, Atms.	Time, Min.	T., °C.	p, Atms.	Time, Min.	T., °C.	p, Atms.	Time, Min.	T., °C.	p, Atms.	Time, Min.	T., °C.	p, Atms.	Time, Min.	T., °C.	p, Atms.	Time, Min.	T., °C.	p, Atms.
0	375	10	10	375	8	0	365	10	0	330		0	360	12	0	360	8	0	350	5
10	420	28	10	435	30	10	435	30	10	360	11	10	420	32	10	430	31	10	430	22
20	475	42	20	480	43	20	480	39	20	420	31	20	460	43	20	460	41	20	435	27
30	515	56	30	515	52	30	500	43	30	460	42	30	485	50	30	465	43	30	440	33
40	545	85	40	540	62	40	520	50	40	485	51	40	500	53	70	478	45	40	445	35
50	572	141	50	565	92	50	540	60	50	500	60	50	495	55	100	478	48	60	445	35
55	585	172	55	575	139	55	540	68	60	495	71	60	495	52	160	479	55	100	445	35
60	600	199	60	575	165	60	535	71	70	495	85	90	515	69	220	480	70	180	440	35
70	620	239	70	580	212	70	538	78	80	515	101	120	510	92	280	480	78	200	445	35
80	625	267	80	580	227	80	538	84	90	510	112	180	510	126	300	480	78	240	445	35
90	625	286	90	580	237	140	538	128	150	510	153	210	510	138	300	480	80	270	445	35
110	625	291	100	580	242	200	540	165	215	510	176	220	510	138						
110	625	298	120	575	248	220	540	183	215	510	176	220	510	138						
145	625	318	120	575	248	220	540	183	215	510	176	220	510	138						

grams of zinc was placed in the apparatus but since the experiment with zinc showed that this metal has no special catalytic action in the presence of iron, these experiments will not be described.

The curves of pressure increase XII to XVIII (Fig. 4) for isoamyl alcohol at various temperatures appear similar to those for other alcohols and consist of three branches which become more pronounced at the higher temperatures. It should be mentioned that there is no part of the curve for isoamyl alcohol which is parallel to the abscissa axis. This was due to the fact that after the alcohol decomposed into hydrogen and isovaleric aldehyde and the latter split into isobutane and carbon monoxide, the decomposition of this saturated hydrocarbon into methane and propane (and partially into ethane) proceeded slowly, with hydrogen participating also in this decomposition:



Thus, there is this third reaction which proceeds very slowly. If those points are marked on the curve at which the pressure increases very slowly (one to two atmospheres in five minutes), and if under these conditions the decomposition of alcohol is considered to reach completion according to two equations, and the pressure corresponding to this point on the curve be called the maximum pressure, $p_{\max}$, then the constant K of decomposition for isoamyl alcohol can be calculated.

In the decomposition of isoamyl alcohol at 625° (Expt. 236, Curve XII), $(dp/dt)_{\max}$ is equal to 6.2 kilos per minute and since the time t during which the maximum pressure was reached may be considered 140 minutes, taking into consideration the assumption mentioned above, the constant K is equal to $(dp/dt)_{\max} \cdot t$ = 868 kilo minutes.

For Experiment 340 (Curve XIII), at a maximum temperature

TABLE 10

Experiment No.	Time, Min.	T., °C.	Max. Press., Atms.	Final Press., Atms.	Catalyst	Analysis of Gas in %						Amount of Gas, L.	Amount of Liquid, G.
						C_nH_{2n}	CO_2	O_2+N_2	CO	H_2	C_nH_{2n+2}		
267	60	510	atm.		Fe	11.0	1.2	1	9.4	63.8	13.6	34.000	55 g. aldehyde
269	60	535	atm.		Fe							40.500	1 g. carbon
266	60	570	atm.		Fe	11.8	1.2	1	12.0	60.0	14.8	40.500	3 g. carbon
350 Curve XI	190	540	119	17	No catalyst	6.0	4.2	1.6	23.8	27.0	37.4	3.600	22
227	180	430	High pressure		Fe	2.2			1.8	90.4	5.6	0.500	
228	180	460			Fe	2.4	3.3		10.2	74.5	9.6	1.000	
232	180	500			Fe	2.2	1.8	1.8	32.8	35.8	25.6	4.000	
233	180	510			Fe	3.8	1.9	1.1	29.0	21.9	42.3	7.000	
234	155	520			Fe	4.3	2.0	0.8	32.8	19.1	41.0	9.600	
235	140	580			Fe	6.9	6.9	0.8	7.8	6.7	71.0	21.500	
236 Curve XII	150	625	318	81	Fe	2.0	6.8	1.0	5.8	5.4	79.0	27.900	
340 Curve XIII	130	580	298	60	Fe	1.8	5.0	1.2	14.0	7.0	71.0	22.950	2
341 Curve XIV	220	540	183	40	Fe	4.0	8.0	1.0	16.0	15.4	55.6	14.850	6
342 Curve XV	210	520	176	33	Fe	4.0	6.2	1.2	19.8	10.0	58.8	13.350	12
343	210	510	138		Fe	5.4	3.6	1.0	27.0	12.0	51.0	8.850	24
344	300	480	80	8	Fe	6.2	1.8	1.6	28.8	17.0	44.6	2.250	33
352	780	440	35		Fe								

of 580°, $(dp/dt)_{\max} = 6.6$ kilos per minute; $t = 135$ minutes and $K = 798$ kilo minutes.

For Experiment 341 (Curve XIV), at a maximum temperature of 540°, $(dp/dt)_{\max} = 1.6$ kilos per minute, and the time required to reach $p_{\max}$ must be about eight hours. The experiment lasted for four hours and the pressure continued to increase for this temperature in a corresponding way.

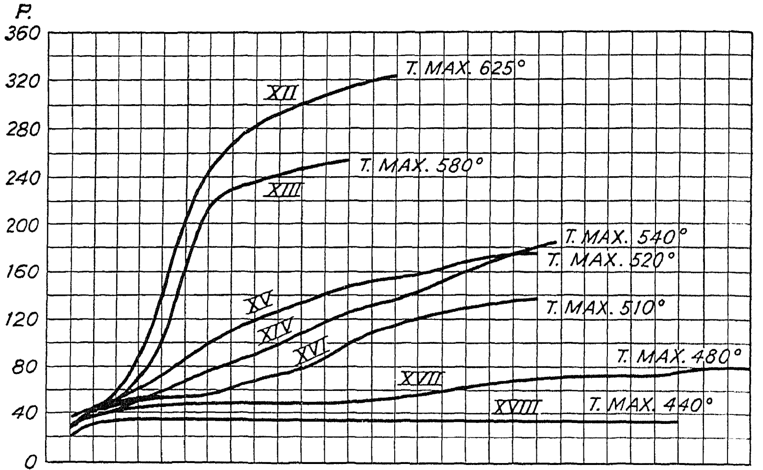


FIG. 4

The decomposition of isoamyl alcohol at other temperatures occurs more slowly than that of ethanol. In general, isoamyl alcohol decomposes under the influence of an iron catalyst more slowly than ethyl alcohol. The above table summarizes all the data on the decomposition of isoamyl alcohol at ordinary and high pressures.

In Experiment 350 (Curve XI) in the above table, the decomposition of isoamyl alcohol in a copper tube was much different from that which occurred in the presence of iron. At high pressure in the presence of iron, isoamyl alcohol decomposes chiefly into hydrogen and aldehyde and the latter into saturated hydrocarbons and carbon monoxide. The effect of high pressure is that with increase in both pressure and time of decomposition of alcohol, the production of carbon monoxide and hydrogen diminishes, but the formation of saturated hydrocarbons increases. The liquid obtained by the decomposition of isoamyl alcohol consists of isovaleric aldehyde, the amount increasing with rise in decomposition temperature up to a certain limit above which the yield of aldehyde decreases. Also, small amounts of amylene and water are formed in quantities which increase with rising temperature. As with other alcohols, carbon formation is not observed in the presence of the catalysts iron and zinc. Besides the products mentioned, a small quantity of condensation products was formed but this was not investigated further. It was noted that the lower the decomposition temperature of the alcohol, the greater the proportion of ethane and propane present in the saturated hydrocarbons formed.

Methyl Alcohol

Methyl alcohol, although it belongs to the class of primary alcohols, has the distinction from other primary alcohols that its primary alcoholic group, (CH_2OH), is bound not to a radical but to hydrogen.

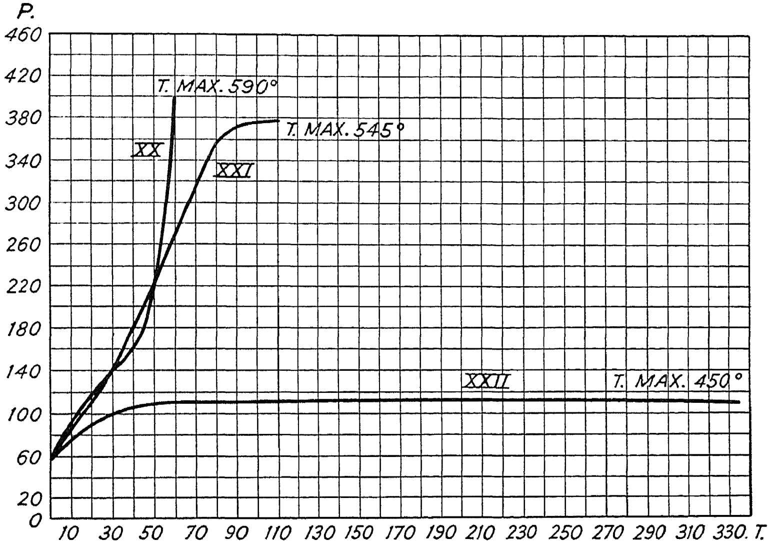


FIG. 5

The decomposition of methyl alcohol was made in an iron tube at 590°, 545°, and 450°. At 450° the decomposition of methyl alcohol barely started, and stopped after a pressure of 112 atmospheres was reached. At 590° methyl alcohol decomposed with enormous speed. At 545° the speed of its decomposition approached that of other alcohols.

Tables XX, XXI, and XXII give the changes of temperature and pressure during the decomposition of 40 grams of methyl alcohol.

TABLE 11

Table XX, Curve XX			*Table XXI, Curve XXI*			*Table XXII, Curve XXII*		
Time, Min.	T., °C.	p, Atms.	Time, Min.	T., °C.	p, Atms.	Time, Min.	T., °C.	p, Atms.
0	405	50	0	405	45	0		48
10	450	88	10	450	84	20	418	91
20	490	117	20	495	112	40	437	107
30	515	139	30	527	198	60	447	107
40	545	164	40	540	175	95	446	108
45	560	188	50	548	223	155	450	111
50	575	228	60	547	280	215	450	112
55	585	292	65	550	312	275	450	113
60	590	400	70	545	335	365	450	113
			110	540	376			

From Table XX it is seen that $(dp/dt)_{\max}$ = about 20 kilos per minute, and because the decomposition occurred within 60 minutes, the constant K would be 1200 k.m. which considerably exceeds the constant for other alcohols.

Table XXI shows that $(dp/dt)_{\max} = 6.4$ kilos per minute. The time (t) required to reach the pressure $p_{\max}$ of 376 atmospheres was 100 minutes and therefore, K equals 640 k.m. At this and lower temperatures the constant K approaches the value characteristic of other alcohols.

Table 12 summarizes the results on the decomposition of methyl alcohol.

It is interesting that the gaseous decomposition products of methyl alcohol are free from olefins and rich in methane. Decomposition of methyl alcohol at ordinary pressure gives gas of the following composition: H_2, 72%; CO, 25%; CH_4, 3%.

Clearly, it can be concluded that carbon monoxide is reduced to methane under pressure in the presence of catalytic iron.

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

Acetaldehyde

In order to show the decomposition of aldehyde under pressure an experiment was made in the presence of iron. In one of the

TABLE 12

EXPT. No.	CURVE No.	TIME, MIN.	T., °C.	PRESS., ATMS.		CATALYST	ANALYSIS OF GASES IN %						GAS PRODUCED, L.	LIQUID RECOVERED, G.
				Max.	Final		C_nH_{2n}	CO_2	O_2	CO	H_2	C_nH_{2n+2}		
359	XX	80	590	400	114	Fe		12.2	1.6	9.6	37.8	38.8		10
360	XXI	125	545	376	105	Fe		12.0	1.2	9.2	38.2	39.4	25.5	12

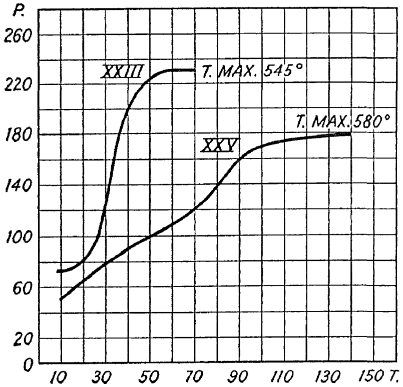


FIG. 6

TABLE 13

Table XXIII, Curve XXIII

TIME, MIN.	T., °C.	p, ATMS.
0	365	48
10	425	68
20	475	82
30	545	138
35	530	181
40	545	211
50	550	232
60	545	232
70	545	225
75	545	218

experiments, the value $(dp/dt)_{max}$ for acetaldehyde was equal to 8.6 kilos per minute (Table 13), and the time, t, during which the pressure p_{max} was reached was equal to 50 minutes. Thus, K was equal to 430 k.m., which is about one-half as much as for alcohols. The pressure decreased after one hour of heating because a side reaction, polymerization of ethylene (see later) started. After cooling, the pressure in the bomb was 60 atmospheres.

A volume of 16.25 liters of gas and 12 g. of liquid were obtained. Analysis of the gas gave the following results: CO_2, 19.4%; C_nH_{2n}, 3.0%; O_2, 1.6%; CO, 17.4%; H_2, 9.6%; C_nH_{2n+2}, 49%. The lower carbon monoxide content of these gases distinguishes them from those formed by the decomposition of aldehydes at ordinary pressures.

The decomposition of acetaldehyde into saturated hydrocarbons and carbon monoxide proceeds at high velocity, but a reaction takes place between the gases which accounts for the fact that carbon monoxide disappears and carbon dioxide accumulates. Most of the recovered liquid distilled at 70–80°, and was unsaturated in character as was also the corresponding material obtained from ethyl alcohol.

Secondary Alcohols

Decomposition of Acetone and Dimethyl Carbinol

The secondary alcohol, isopropyl alcohol, boiling point 80–81°, decomposes in the high pressure apparatus in the presence of an iron catalyst in a different way from that observed for primary alcohols. Table XXIV indicates the course of decomposition of isopropyl alcohol and Table XXV that of acetone.

For isopropyl alcohol $(dp/dt)_{max}$ was not large, namely, 2.5 kilos per minute at the high temperature of 615°, and, therefore, complete decomposition and attainment of p_{max} might be expected only after a long time of heating. The products indicated that the secondary alcohol decomposes into hydrogen and acetone, the latter undergoing further decomposition. After cooling, the pressure was 42 atmospheres. The 12.1 liters of discharged gas had the following composition: CO_2, 4.6%; C_nH_{2n}, 1.8%; O_2, 1.6%; CO, 4.0%; H_2, 15.0%; C_nH_{2n+2}, 72.8%. The saturated hydrocarbons consisted of ethane and methane. Twenty-

TABLE 14

Table XXIV. Isopropyl Alcohol			*Table XXV. Acetone*		
Time, Min.	T., °C.	*p*, Atms.	Time, Min.	T., °C.	*p*, Atms.
0	330	10	0	330	31
10	460	40	20	440	69
60	565	100	40	520	90
70	580	109	70	540	120
75	590	115	75	560	130
80	600	128	80	580	141
90	602	150	90	580	160
100	602	171	100	580	169
110	603	192	140	580	180
135	615	240			

three grams of liquid was recovered, about one-half of which was acetone mixed with undecomposed alcohol, water, and a small amount of condensation products.

Decomposition of Acetone

Curve XXV showed that this reaction proceeded much more slowly than that of acetaldehyde. Here $(dp/dt)_{\max} = 2.2$ kilos per minute, which is approximately the same as that for isopropyl alcohol. Constant K was not calculated because the experiment was not completed. On cooling, the pressure was 38 atmospheres. The 10.9 liters of gas produced analyzed as follows: CO_2, 19.2%; C_nH_{2n}, 1%; O_2, 0.6%; CO, 1%; H_2, 11.6%; C_nH_{2n+2}, 66%. The saturated hydrocarbons consisted chiefly of methane with small amounts of ethane. From the 19 grams of recovered liquid, low boiling products of an unsaturated character were separated.

Decomposition of Dimethylethyl Carbinol

Dimethylethyl carbinol when passed through an iron tube under ordinary pressure decomposed only above 600°. This high stability shows that tertiary alcohols are sharply distinguished from primary and secondary alcohols. Among the products of decomposition are water and amylene, the latter beginning to decompose into gas at this temperature. Dimethylethyl carbinol, heated in a closed vessel in the presence of iron catalyst, undergoes a similar decomposition at the high temperature of 605–610°, but because amylene polymerizes readily at this temperature the net result was a mass of thick tar and water in the iron bomb. The course of decomposition is shown in Table 15.

TABLE 15

Table XXVI

TIME, MIN.	T., °C.	p, ATMS.
0	365	13
10	422	31
40	527	67
60	565	100
70	585	119
75	595	132
80	605	151
85	612	170
90	615	182
110	625	207
120	625	211

For the above reaction $(dp/dt)_{\max} = 3.8$ kilos per minute. The time (t) for reaching $p_{\max}$ was 120 minutes and constant K was calculated as 486 k.m. On cooling, the pressure in the apparatus dropped to 46 atmospheres. The 14.3 liters of gas collected had the following composition: CO_2, 2.0%; C_nH_{2n}, 4.0%; O_2, 1.4%; CO, 0%; H_2, 36%; C_nH_{2n+2}, 89%. The gas was rich in methane and ethane; but carbon monoxide was absent, a fact very characteristic for tertiary alcohols which are unable to give either an aldehyde or a ketone on decomposition. The 5 g. of liquid recovered consisted of water and a thick tar.

CONCLUSIONS

By observing the constants K for several alcohols, it is seen that they are clearly different for the three classes of alcohols. For primary alcohols, the value K is close to 800 kilo minutes; for secondary alcohols, in spite of the high temperature and the prolonged heating, the value obtained for K is less than half as great as for primary alcohols; for tertiary alcohols the value is approximately one-half that of the primary alcohols. What is the explanation for this difference in the magnitude of K for various alcohols? It may be assumed that this difference finds its explanation in the ability of the alcohols to undergo definite decomposition under the influence of catalysts and in the stability of the products formed. The primary alcohols are able to decompose into aldehyde and hydrogen under the influence of iron, but the aldehydes in the presence of this catalyst suffer further decomposition; as a result, two reactions proceed. First, from one molecule of alcohol two molecules are formed; and from one of these molecules, two others are formed. These two reactions are caused by the application of heat in the presence of a catalyst. For these two reactions the product of the maximum velocity of the increase of pressure and the time interval during which the maximum pressure was reached is twice as great as that observed when aldehyde splits into carbon monoxide and methane by a single decomposition reaction.

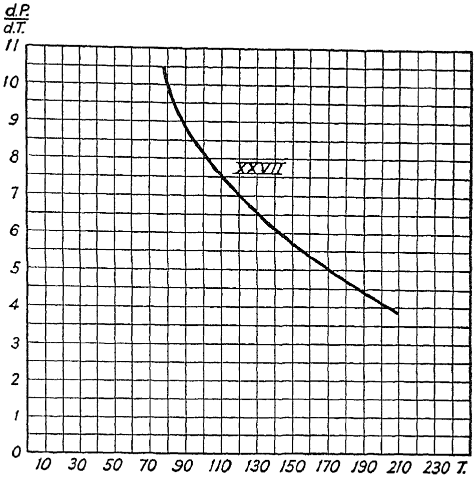


Fig. 7

In just the same way the catalytic decomposition of secondary alcohols in the presence of iron which yields ketones, substances which are more stable than aldehydes, must have a constant *K* about one-half as large as that of the primary alcohols. Such a decomposition was observed for isopropyl alcohol.

Finally, the tertiary alcohols are stable to decomposition under the influence of iron at ordinary as well as at high pressures. With dimethylethyl carbinol the derivative $(dp/dt)_{\max}$ reaches a maximum only at very high temperatures and even then the decomposition proceeds very slowly. Here a partial decomposition of the alcohol produces water and amylene, but the tertiary alcohol decomposes mainly into saturated hydrocarbons and water. For the primary alcohols, except methyl alcohol, the constant *K* has quite narrow limits. By plotting the time corresponding to the attainment of maximum pressure, against $(dp/dt)_{\max}$ for various alcohols, an equilateral hyperbola (see Curve XXVII) is obtained.

The data presented are not sufficient to justify the drawing of a final conclusion, but these rough generalizations, made on the basis of the facts obtained, indicate that the decomposition of organic compounds under high pressure in a closed vessel exhibit certain regularities which escaped previous observation and that a study of these regularities would probably enable us to understand many theoretical questions concerning the decomposition of organic compounds.

Although these investigations on alcohol decomposition were made almost thirty years ago, since then very little scientific material has been added to this field. With the introduction of *activation energy* into the sphere of kinetic chemical reactions at the present time, I suggest that it would be of interest to apply the equation of Arrhenius:

$$K = K_0^{-Q/RT} \tag{1}$$

where Q is the activation energy, T the absolute temperature, K_0 the constant for the given velocity of the reaction, R the gas constant, and K the constant of the reaction velocity. By using the increase in pressure instead of the velocity constant of the reaction (in our case, the decomposition of alcohol), the equation might be written as follows:

$$\log_e K = -Q/RT + \tag{2}$$

If the decomposition of alcohols up to a certain temperature should produce only aldehydes and hydrogen, equation (2) would represent a linear relationship between $\log K$ and $1/T$.

From the equation of this straight line it would be possible to calculate the tangent angle of the inclination and to determine the activation energy for the given reaction. By means of this more refined method we would also be able to test the assumption that the activation energy depends only on the chemical tension of the catalyst and that it does not depend upon the nature of the alcohol.

Probably, we would have the same relationship for the decomposition of alcohols which was developed in its general features by the application of the method of measuring $(dp/dt)_{\max}$ in the investigation of the decomposition of alcohols under pressure.

But it is known that aldehyde might decompose easily into hydrocarbons and carbon monoxide and that the velocity of this reaction will depend, of course, on the temperature and chemical properties of the catalyst. However, we could take such a temperature and choose such a catalyst that the molecule of alcohol would decompose at once according to the equation:

$$CH_3CH_2OH \rightarrow CH_4 + CO + H_2$$

This reaction with production of these three gases in equal volumes was actually observed in the decomposition of alcohols when passed through a platinum tube.

It would appear interesting to study the kinetics of these catalytic reactions under pressure with alcohols, as well as with aldehydes, in order to determine their activation energy which, without doubt, is of great interest because of its significance in judging the mechanism of the reactions and especially catalytic reactions.

Up to the present time the study of the kinetic dehydrogenation of alcohols has been carried out by Palmer and Constable at ordinary pressure in the presence of a reduced copper catalyst. The results obtained by these authors are summarized as follows:

The velocity of hydrogen liberation depends neither upon the velocity at which the substance is passed through the catalyst nor upon the pressure; it is a reaction of zero order. The dependence of the reaction velocity on temperature is expressed by the formula of Arrhenius.

The value of the activation energy, depending on the temperature of the reduction of the catalyst, varies from 22,000 to 25,000 cal. per mol. and is the same for ethyl, propyl, butyl, isobutyl, and isoamyl alcohols.

When working with one and the same preparation of copper catalyst, the absolute values of the velocity of dehydrogenation of these alcohols are equal.

Similar conclusions were reached also by Zelinsky and Pavlov. They investigated the kinetics of dehydrogenation of various hydroaromatic hydrocarbons and found that the activation energy does not change for various hydrocarbons and also heterocyclic compounds, namely, decahydronaphthalene, cyclohexane, piperidine, and others; it is the function only of the chemical nature of the catalyst employed. The conclusions indicated find their confirmation in Table 16.

Having at the present time perfected methods for the investigation of reactions under high pressures, it seems to be extremely interesting to study the energy of activation for the most simple reactions of organic substances under pressure.

TABLE 16

COMPOUND	CATALYSTS			
	Pt. Carbon	Pt. Asbestos	Pt. Asbestos	Pt. Asbestos
Decahydronaphthalene	18.890	18.990		9.990
Cyclohexane	18.040	18.040	15.300	9.710
Piperidine	19.990	18.460	15.760	
Average, Cal. per mol.	18.990	18.460	15.530	9.850

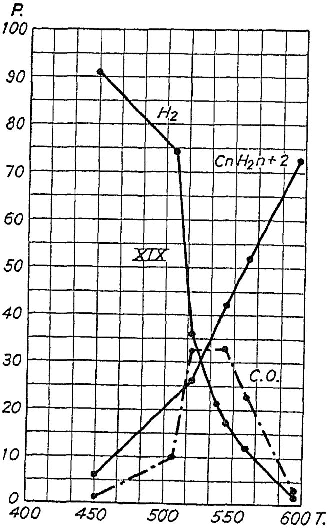


FIG. 8

Further, I cannot avoid indicating one side of the matter which, according to my opinion, deserves special attention. In the decomposition of all organic compounds studied it is observed that with increase in pressure and also in time of heating the gases formed become poorer and poorer in carbon monoxide and hydrogen, but at the same time richer in saturated hydrocarbons (Curve XIX, Fig. 8). This circumstance, I think, may have significance for those who explain the origin of petroleum in nature as due to the decomposition of organic substances of the animal and plant kingdom. For example, the organic hypothesis of the origin of petroleum was advanced mostly by Engler who showed in his experiments that according to all probability petroleum originated by the decomposition of fats. In a special chapter, "The Question of the Origin of Petroleum," the reactions which served as the foundation for the mineral hypothesis of the origin of petroleum (D. I. Mendeléeff) and the organic hypothesis (Engler) will be discussed in detail, but now it will be merely indicated that in the experiments of Engler on the decomposition of fats under pressure, the gases resulting from the reaction contained about 30% of carbon monoxide and a large volume of hydrogen. Since petroleum gases are almost always free from carbon monoxide and hydrogen this fact represents an inadequacy of Engler's hypothesis on the origin of petroleum. However, after I made experiments on the decomposition of organic compounds under pressure, it was found that carbon monoxide and hydrogen react with each other under pressure in the presence of the catalyst iron and give methane and that an accumulation of paraffinic hydrocarbon takes place; therefore these objections against Engler's theory had to be dropped. Dr. Engler focused his attention on my experiments and used these results as confirmation of his theory. Besides this, my experiments showed that in order to clarify the very important question as to the properties of petroleum, temperature, pressure, and catalytic processes should be considered which could exist either during the formation of petroleum or during its storage in the depths of the earth.

CHAPTER II

DEHYDRATION OF ALCOHOLS

In the pyrogenetic decomposition of various alcohols under the influence of the contact agents previously investigated we consistently observed the decomposition of alcohol mainly into aldehyde and hydrogen, but there was also a second significant decomposition of the alcohol in another direction—into olefin and water. On examining the results of the pyrogenetic decomposition of alcohols occurring in glass and platinum tubes, we see that the amount of alcohol converted into olefin and water is a considerable part of the alcohol decomposed, although the decomposition of the alcohol is mainly into aldehyde. According to my experiments, the decomposition of ethyl alcohol in the presence of zinc dust at 550° proceeds equally in two directions—into aldehyde and hydrogen, and into ethylene and water. Experiments of Nef [1] showed that a similar decomposition of isoamyl alcohol occurs at 380–420° in the presence of zinc dust and pumice.

Thus, it appeared interesting to find a catalyst which would force alcohols to decompose in only one direction—into ethylene hydrocarbon and water. I will describe briefly the manner in which I was led to the discovery of such a catalyst.

During my first experiments on the decomposition of alcohols under the influence of an iron catalyst, as already mentioned, I tried to determine what was the actual catalyst in the aldehyde decomposition of alcohol—whether it was the iron itself or the carbon which separated during the reaction. I carried out various experiments with this object in mind, and in one of these I employed a graphite tube,[2] made especially for the purpose, which contained the *highest possible content of graphite,* in order to find out about the influence of carbon upon the decomposition of alcohol. A binder was necessary in the fabrication of the tube and for this purpose kaolin had been used, but at that time I did not attach catalytic significance to this kaolin and I do not think that others did—my attention was focused upon the influence of graphite upon the decomposition of alcohols. The graphite tube was placed inside an iron in such manner that the vapors of alcohol could not come in contact with iron.

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[1] Nef, Ann., *318*, 217 (1901).

[2] The graphite tube was made in the Morgan crucible plant in St. Petersburg.

I made the first experiment in December, 1901, in the laboratory of the Artillery Academy. Ethyl alcohol was passed through the graphite tube at 600° and it was at once evident that an entirely different reaction was taking place. The exit gas, on being bubbled through bromine, yielded pure ethylene bromide. The liquid in the receiver consisted only of water and a small amount of undecomposed alcohol together with a slight trace of aldehyde scarcely detectable by means of a silver mirror. This experiment indicated, first, that iron and not carbon is the catalyst of the aldehyde decomposition of alcohol and second, that there is a new catalyst in the graphite mass, which produces a specific decomposition of alcohol into olefin and water. A series of experiments carried out on the decomposition of other alcohols in a graphite tube confirmed the possibility of an exclusive catalytic decomposition of alcohol into olefin and water and on the 23rd of December, 1901, at the meeting of the Naturalists' and Physicians' Section of Chemistry [1] in St. Petersburg, I gave a paper on the possibility of two kinds of catalytic decomposition of alcohols. The necessity of making clear which of the components of the graphite tube—graphite, silica, or alumina—was the catalyst in the ethylene decomposition of alcohol was realized. The first experiments on the olefinic decomposition of alcohol were made in a graphite tube, but soon it was evident that the dehydration of alcohol is caused by alumina, and that a temperature of 360° is necessary for this catalytic reaction. If kaolin is used a somewhat higher temperature, about 450–500°, is required.

Up to the end of 1901, the time of the discovery of the catalytic ethylene decomposition of alcohol in a graphite tube, which offered the possibility of complete decomposition of alcohol into ethylene and water, there existed only one observation on this reaction in the literature. This observation (which had been completely forgotten, not even being mentioned in Beilstein's Handbuch) was made at the end of the 18th century by four Dutch chemists, Deimann, Van Trootswyk, Lauwerenburg, and Bondt,[2] who made the statement that the vapors of ethyl alcohol are decomposed by kaolin into gases in which ethylene predominates. They gave no indication of the temperature required, of the yield of ethylene, nor the manner of experimentation.[1]

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[1] The meeting of the section of chemistry took place in the chemical auditorium of the Artillery Academy.

[2] Deimann, Van Trootswyk, Lauwerenburg, and Bondt: Ann. Chim. Phys., *21*, 58 (1797); Ann. Physik, *2*, 208 (1799).

The study of the component parts of the graphite tubes as catalysts led me to the firm opinion that alumina and kaolin are the real catalysts of the ethylene decomposition of alcohol. But it was the study of the influence of catalysts upon the pyrogenetic decomposition of alcohols that led me to the discovery of the catalyst alumina [2] and caused me to propose its use as a general method for obtaining olefins from alcohols—aliphatic as well as cyclic. This method has been adopted not only in the laboratory, but also in industrial practice. It was only after these systematic investigations that the rôle and significance of alumina as catalyst in organic chemistry became clear.

Decomposition of Alcohols in a Graphite Tube

It is well known that graphite crucibles consist chiefly of kaolin and graphite with small amount of iron. This complex mixture has no action upon alcohols under ordinary laboratory conditions but it proved to be active in the pyrogenetic decomposition of alcohol. It may be added, that with alcohols in general, only traces of their aldehyde decomposition products are found, these traces perhaps being due to iron oxide and the air present in the apparatus at the beginning of the experiment.

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[1] Besides this, at the March, 1901, meeting of the Russian Physical Chemical Society, a very brief communication was presented by V. E. Tischenko and his coworker student Gregoriev, that ethyl and isobutyl alcohols decompose when heated in a tube with alumina. The ethyl alcohol was heated in anthracene vapors and the isobutyl alcohol in vapors of diphenyl amine. The hydrocarbons in the gas were chiefly olefins. This observation was contained in a very brief remark of a few lines published in the protocols of the Journal of the Russian Chemical Society and not published in any other article. It appeared after my paper on "Pyrogenetic Reactions with Organic Substances" which I presented at the January meeting of the Russian Physical Chemical Society in 1901, in which I indicated the rôle of catalyst in the decomposition of organic compounds.

From this protocol note no conclusions could be drawn concerning the catalytic decomposition of alcohols, because the temperature of 350° (temperature of anthracene vapors) would scarcely be sufficient for an extensive decomposition of ethanol into ethylene and water, as shown by our investigations. The gas was not analyzed, the preparation or source of the alumina was not indicated, nor were any of the operating conditions of the experiment given, such as the charging rate of the alcohol. Since the authors made no further attempt to follow up this observation, we are justified in concluding that they meant only to draw attention to an interesting but isolated experiment, and that they were far from any idea as to the real significance of the observation. If they had considered alumina to be a catalyst, their next step would have been to prove that a small amount of alumina is capable of decomposing a large amount of alcohol and that the percentage of ethylene in the gases remains constant throughout the life of the catalyst.

This note of Gregoriev had no influence upon the development of my scientific investigations on catalysis and by the end of 1901 I had discovered that alumina caused complete decomposition of ethanol into ethylene and water.

[2] Ipatieff, Ber., *35*, 1058 (1902).

In the report concerning the results of the experiments in the graphite tube I stated[1] that it had not yet been determined whether the whole mass of the graphite tube or only one of its components were acting as catalyst in the ethylene decomposition of alcohols. Only later experiments have shown that pure graphite (free from iron) did not catalyze the decomposition of alcohol into water and ethylene.

Further experiments described in this book will show which substance acts as catalyst.[2]

Decomposition of Ethyl Alcohol

Energetic decomposition into ethylene and water took place when ethyl alcohol vapor was passed through a graphite tube (or through a glass tube filled with pieces of broken graphite tube) heated at 600°. In the heating, the graphite tube was placed in one of iron. The graphite did not change in weight and retained its catalytic activity for a long time. It may be used for other alcohols as well as for ethyl alcohol. During 30 minutes 140 g. of alcohol was passed through a glass tube filled with pieces of graphite; about half of the alcohol was decomposed. The analysis of the gas was:

$$C_nH_{2n},\ 94.6\%;\ CO,\ 0.2\%;\ H_2 \text{ and } CH_4,\ 6.2\%$$

The gas on being passed through bromine at 0° gave 160 g. of pure ethylene bromide with boiling point 130–131°. Only a trace of the aldehyde was formed.

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[1] Ipatieff, J. Russ. Phys. Chem. Soc., *33*, 182 (1901); *34*, 143 (1902).

[2] P. Sabatier in his book "Die Katalyse in der organischen Chemie" published in 1927 (Leipzig) makes the erroneous statement on p. 212 that Gregoriev, in his brief note was able to show that metal oxides, in general, possess the property of removing water from alcohol, but Gregoriev tested only one material—alumina—and therefore was unable to draw any conclusions about oxides in general. Moreover, all metal oxides do not possess this property. Sabatier further states that Ipatieff confirmed this experiment in a graphite tube but this does not agree with the facts. Why should I employ a graphite tube in order to confirm Gregoriev's experiment on alumina? Had I been occupying myself merely with the repetition of Gregoriev's experiment I would have taken alumina and placed it in a glass tube.

Decomposition of Propyl Alcohol

One hundred and twenty-seven grams of propyl alcohol was passed over the catalyst in 30 minutes at 600°; half of the alcohol was decomposed into propylene and water. The gas passed through bromine at 0°, producing 160 grams of pure propylene bromide boiling at 141–142°. Analysis of the gas showed it to contain:

$$C_3H_6,\ 93\%;\ CO,\ 0.4\%;\ H_2,\ 2.4\%;\ CH_4 \text{ and } C_2H_6,\ 3.4\%$$

Decomposition of Isoamyl Alcohol

Isoamyl alcohol vapor (147 g.) was passed through a graphite tube during 35 minutes; 70 g. of amylene and 30 g. of water were obtained, the remainder of the product being undecomposed alcohol. No gas was liberated. Using a short time factor a large amount of amylene may be obtained from isoamyl alcohol by operating at such a temperature that no gas is liberated.

Decomposition of Dimethylethyl Carbinol

The tertiary alcohol, $(CH_3)_2C(OH)C_2H_5$, decomposed completely in a graphite tube at 600°. In 25 minutes, 96 g. of alcohol gave 30 g. of water and 60 g. of amylene boiling at 30–40°. According to the boiling point, the amylene obtained consisted of two hydrocarbons, trimethylethylene and unsym-methylethylethylene, the formation of which can be explained by removal of water in two ways:

$$(CH_3)_2C(OH)CH_2CH_3{-}H_2O \cdot \quad \cdot\ (CH_3)_2C{=}CHCH_3$$
$$(CH_3)_2C(OH)CH_2CH_3{-}H_2O \cdot \quad (CH_3)(C_2H_5)C{=}CH_2$$

No gas was liberated in this reaction.

Decomposition of Methyl Alcohol

It was interesting to investigate the action of the graphite tube upon methyl alcohol, from which ethylene could not be formed directly by the splitting out of water. Experiments showed that abundant decomposition was promoted by the graphite contact. One hundred and twenty-six grams of alcohol underwent about 50% conversion into gases within 45 minutes at 650°. The composition of the gas from the graphite tube was markedly different from that resulting from the decomposition of methanol in an iron tube.

	Graphite Tube	Iron Tube
C_nH_{2n}	2.8%	
CO	12.8%	24.6%
CH_4	39.2%	4.5%
H_2	45.2%	70.0%

The gas contained considerable methane, which was not the case in the iron tube. Therefore, this might be called the *methane decomposition* as distinguished from the *aldehyde decomposition.* When these experiments were made it was impossible to say why methane was formed. At the present time this decomposition might be explained by the following equations:

$$(1)\quad 2CH_3OH \rightarrow CH_3OCH_3 + H_2O$$

$$(2)\quad CH_3OCH_3 \rightarrow CH_4 + CO + H_2$$

$$(3)\quad CH_3OCH_3 \rightarrow C_2H_4 + H_2O$$

First, methyl ether is formed, which decomposes partly according to equation (2) to yield methane and partly according to equation (3) to yield ethylene. This mechanism was later confirmed experimentally.

Decomposition of Isobutyl Alcohol

Isobutyl alcohol (boiling point, 107–109°), when passed through a graphite tube at 500–550°, decomposes into isobutylene and water with no formation of isobutyric aldehyde. In order to obtain pure isobutylene it is only necessary to regulate the velocity of the alcohol vapor.

Of the 197 g. of alcohol passed through the graphite tube at 550° during 30 minutes, 80 g. decomposed. Analysis of the gas showed:

$$C_4H_8,\ 94\%;\ CO_2,\ 0.4\%;\ CH_4,\ 4.5\%;\ H_2,\ 1.5\%$$

In another experiment, 440 g. of alcohol was passed through a graphite tube during 70 minutes at the same temperature. Seventy liters of gas was formed of which 95% was isobutylene.

Since up to this time it had been impossible to obtain pure isobutylene by removing water from isobutyl alcohol, it was interesting to investigate the homogeneity of the butylene obtained by the catalytic method. According to the investigation of Favorsky and Desbout,[1] the butylene obtained from isobutyl alcohol by the action of zinc chloride (method of Lebel and Greene [1] consists of a mixture of two isomers—66% being isobutylene and 34% being alpha- and beta-butylenes. Butylene obtained according to the method of Puchot [2] from isobutyl alcohol by the action of sulphuric acid is also non-homogeneous, as shown by Konovalov.[3]

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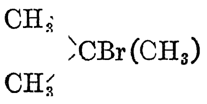
[1] Favorsky and Desbout, J. prakt. Chem., [2], *42*, 152–154 (1890).

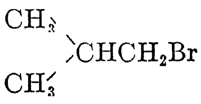
The preliminary experiments on the decomposition of isobutyl alcohol in a graphite tube showed that the resulting isobutylene was not pure, but was mixed with alpha- and beta-butylenes. Shortly thereafter I showed that it is impossible to judge the homogeneity of isobutylene or of other olefins on the basis of the addition of hydrogen bromide in acetic solution.[4]

To determine the purity of the isobutylene obtained by the decomposition of isobutyl alcohol in a graphite tube, the olefin mixture was passed at 0° into a saturated solution of hydrogen bromide in acetic acid. The product obtained was heated with water at 100°, whereby the tertiary bromide dissolved with the formation of trimethyl carbinol and the remaining bromide, insoluble in water, was found to be the primary bromide, boiling at 91–93°. From this experiment it was possible to conclude that the isobutylene was impure and that it contained a certain amount of alpha-butylene.

However, when this method of analysis was tested,[5] it was discovered that a mixed bromide results even when starting with pure isobutylene. In the presence of acetic acid, hydrogen bromide adds to isobutylene in two ways with the formation of two products. Tertiary isobutyl bromide (I) is soluble in water, but primary isobutyl bromide (II) is insoluble.



$$\begin{array}{l}CH_3\\ CH_3\end{array}\!\!>CBr(CH_3)$$



$$\begin{array}{l}CH_3\\ CH_3\end{array}\!\!>CHCH_2Br$$

II

In order to clear up the question as to the purity of the isobutylene obtained by the contact decomposition of isobutyl alcohol in the graphite tube, its reaction with aqueous hydrogen halides and with sulphuric acid was studied.

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[1] Lebel and Greene, Bull. soc. chim., *29*, 306 (1878).

[2] Puchot, Ann. chim. phys., [5], *28*, 508 (1883).

[3] Konovalov, Ber., *13*, 2395, (1880).

[4] Ipatieff, Ogonovsky, Ber., *36*, 1983 (1903); Ipatieff and Dehanov, J. Russ. Phys. Chem. Soc., *36*, 659 (1904).

[5] See a separate chapter on the manner of addition of hydrogen halide acids to olefins.

Isobutyl alcohol (195 g.) was passed at 480–500° through a glass tube packed with graphite and 27 liters of gas was obtained which analyzed 98.9% butylene. Ten liters of the butylene was passed through an aqueous solution of hydriodic acid (sp. gr., 1.96); 9 liters were absorbed and 42 g. of iodide obtained. The iodide boiled at 97–100° and on heating with two volumes of water dissolved without residue with the formation of trimethyl carbinol. Ten liters of this same butylene was led into an aqueous solution of hydrogen bromide saturated at 0°; and 39 g. of bromide, boiling at 72–73°, was obtained which dissolved completely on heating with water.

In another experiment 188 g. of isobutyl alcohol was passed over graphite fragments in a glass tube at 520–540° during 40 minutes with the production of 30 liters of gas of 97% butylene content. Eleven liters of this butylene was liquefied over sulphuric acid (one part by weight of water and three parts of sulphuric acid); after shaking 4 hours and then allowing to stand an additional 4 hours, the material had completely dissolved.

Decomposition of Trimethyl Carbinol

Trimethyl carbinol (70 g.) was passed at the rate of 1.2 g. per minute through a graphite catalyst contained in a glass tube heated at 480°. The alcohol was decomposed completely and 18 liters of gas was obtained which analyzed 99% butylene. By passing the gas through an acetic acid solution of hydrogen bromide at 0° a bromide was obtained, the greater part of which dissolved on heating with water. Starting with 50 g. of the bromide, about 4 g. remained insoluble. The insoluble bromide boiled at 90–92° and was considered to be a primary butyl bromide. Now we know that it was also formed from isobutylene because of the addition of hydrogen bromide to this olefin, according to the second reaction (II).

Thus, experiments carried out on the decomposition of alcohols in a graphite tube indicated a new and convenient method of obtaining olefins from alcohols.

DECOMPOSITION OF ALCOHOLS BY MEANS OF ALUMINA AND KAOLIN CATALYSTS

In order to decide the question as to which of the ingredients of the graphite mass is the catalyst in the olefin decomposition of alcohols, the effects of graphite, silicic acid, and alumina were studied at high temperatures.

When the vapors of ethyl alcohol were passed through a glass tube filled with powdered graphite at 600°, a very slight decomposition occurred. Also a series of experiments carried out with powdered precipitated silica showed that silica was not a good catalyst for the ethylene decomposition of alcohols.

During a period of one hour 150 g. of ethyl alcohol was passed through a glass tube filled with powdered silica and heated to 650°. An insignificant amount (ca. 0.5 g.) of aldehyde and a small amount of gas were formed, 140 g. of alcohol remaining undecomposed.

But when alumina [1] was taken instead of silica, then ethyl alcohol, or other alcohols, were readily decomposed into olefin and water. It was only necessary to regulate the rate at which the alcohol was passed, and the temperature of the alumina in order to obtain practically quantitative decomposition into olefin and water. To maintain the required temperature I constructed a special gas furnace in which the temperature could be maintained constant within 5–7°. This furnace had a temperature range from 200 to 700° and served its purpose well before the advent of the superior present-day electric furnace.

It had long been known that alcohol vapor suffered no decomposition when passed through copper tubes at 600–700° and for that reason I carried out most of the experiments with alumina in copper tubes. Cork stoppers were employed to connect the tube with the rest of the apparatus and the ends of the copper tubes were wound with spirals of lead tubing through which cold water was circulated in order to avoid carbonizing the corks.

Decomposition of Ethyl Alcohol

Prior to the detailed study of the decomposition of ethyl alcohol in the presence of alumina, several blank experiments were made in which ethyl alcohol was passed through glass and copper tubes under the same conditions as used later in the catalytic decomposition of alcohols in the presence of alumina.

One hundred grams of ethyl alcohol was passed through a glass tube at 610–630° during one hour and ten minutes, the air having previously been displaced by nitrogen. Ten grams of alcohol decomposed to form 0.75 g. of ethylene and 9 g. of acetaldehyde, 8 g. of the latter decomposing further into carbon monoxide and methane. Gas analysis gave the following figures:

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[1] Alumina as shown by my experiments must possess certain properties in order to be a catalyst (see further).

$$C_nH_{2n}, 9\%; CO, 21.3\%; H_2, 46.5\%; CH_4, 23.4\%$$

At 500–520° in blank experiments (in the absence of alumina) at the same rate of feed as above, the alcohol remained unchanged.

With alumina in a copper tube, ethyl alcohol begins to decompose into ethylene and water at 360°. The temperature can be raised without danger—in fact, the optimum temperature is 420–450°.

In order to prove that the only reaction taking place was decomposition into ethylene and water—in other words, that there was no decomposition into aldehyde and hydrogen, a special experiment was made in which all the air was first swept out of the system by means of carbon dioxide. A glass tube containing 12 g. of alumina was completely swept out with pure carbon dioxide and then 100 g. of ethyl alcohol was passed over the alumina at 380° during one hour. Twenty-four liters of gas was obtained which analyzed 97.7% ethylene. The gas was passed into bromine and 181 g. of ethylene bromide obtained with a boiling point of 130–131°. About 1 g. of divinyl tetrabromide remained in the distillation flask. The liquid which collected in the receiver during the dehydration reaction consisted of water and unchanged alcohol free from even a trace of aldehyde. This experiment proves that the alumina, under the conditions of the experiment, promotes only the ethylene decomposition of ethyl alcohol. It is only when air is present in the apparatus that acetaldehyde is formed, and then only in amount equivalent to the oxygen content.

Experiments on the decomposition of ethyl alcohol in the presence of alumina showed that this oxide could serve for a long time for the preparation of ethylene. The alumina remained unchanged, and a small quantity of it sufficed to decompose a large quantity of alcohol. Thus I was the first to show that alumina is an excellent catalyst for the decomposition of alcohol into ethylene and water.

Decomposition of Propyl and Isopropyl Alcohols

n-Propyl alcohol is decomposed into propylene and water by passage over alumina at 500° in a copper tube. This procedure constitutes a convenient method for the preparation of pure propylene.

Likewise, isopropyl alcohol is converted into propylene and water, decomposition starting at 360°. Fifty-six grams of isopropyl alcohol was passed over alumina during 30 minutes and 15 liters of gas was obtained containing 96% propylene. The remaining 4% consisted of hydrogen and saturated hydrocarbons. The bromide prepared by passing the gas into bromine at 0°, distilled at 140–142° without residue.

Decomposition of Isobutyl Alcohol

Isobutylene and water are formed readily when the vapors of isobutyl alcohol (boiling point, 107–108°) are passed over alumina at 500° in a copper tube. Subsequent experiments showed that isobutylene was the only olefin formed.

In one experiment 355 g. of isobutyl alcohol was passed over alumina at 500° at the rate of 34 g. per minute; 77 liters of gas was obtained which analyzed 98.4% butylene.

A part of the isobutylene was condensed to a liquid with a boiling point of −5°. Another portion of the butylene was passed into an acetic solution of hydrogen iodide which contained about 60% by weight of hydrogen iodide. Investigations by Ipatieff and Dehanov showed that hydrogen iodide in acetic acid solution adds to isobutylene to give only one product, tertiary butyl iodide, $(CH_3)_2CICH_3$, which dissolves readily in water at ordinary temperature. The olefin obtained by the dehydration of isobutyl alcohol gave a 90% yield of iodide on passing into a solution of hydriodic acid in acetic acid and this iodide dissolved completely when heated with water under a reflux condenser.

A five-liter sample of the same butylene obtained by the catalytic dehydration of isobutyl alcohol was liquefied over sulphuric acid (two parts by weight of sulphuric acid to one of water); after shaking for two hours the butylene had dissolved completely with the formation of trimethyl carbinol.

Another five-liter sample of the isobutylene was passed into a flask containing sulphuric acid (consisting of equal weights of water and acid). After shaking and heating[1] at 30–40° for half an hour, the butylene had dissolved completely with the formation of a tertiary alcohol.

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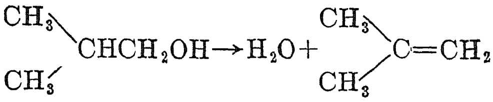
[1] Scheschukov, Ber., *19*, 544 (1885).

The above experiments indicate without doubt that the olefin obtained from isobutyl alcohol by the catalytic method is pure isobutylene and, consequently, that the removal of water from isobutyl alcohol proceeds in one direction only:



$$(CH_3)_2CHCH_2OH \rightarrow H_2O + (CH_3)_2C{=}CH_2$$

I was the first to succeed in obtaining pure isobutylene by the dehydration of isobutyl alcohol.

In all these experiments the amount of aldehyde was so small that it could be detected only by means of the reduction of silver oxide, and the formation of this aldehyde could readily be ascribed to the oxidation taking place at the beginning of the experiment due to the traces of air in the apparatus.

Decomposition of Normal Butyl Alcohol

Normal butyl alcohol obtained from Kahlbaum also decomposed readily into butylene and water in the presence of alumina at 500°. Investigation showed that the resulting olefin consisted chiefly of isobutylene and that normal butylene was present only to the extent of 25–30%. The reason for the non-homogeneity of this butylene is that the normal butyl alcohol from Kahlbaum at this time (1902) contained considerable isobutyl alcohol, as shown by the fact that the iodide prepared from this alcohol by means of iodine and phosphorus contained considerable tertiary iodide. Later, V. Ipatieff, B. B. Corson,[1] and H. Pines [2] had no trouble in producing large quantities of n-butylene from pure n-butyl alcohol in the presence of alumina at 425–450°.

Decomposition of Amyl Alcohol

The greatest number of experiments on catalytic decomposition was carried out with amyl alcohol from fermentation (boiling point, 130–131°). This alcohol decomposes readily into amylene and water, decomposition starting at 350°. In order to show that catalytic decomposition is not caused merely by the combination of the copper tube and a powdered material, one experiment may be mentioned in which isoamyl alcohol was passed through a copper tube packed with ignited, precipitated silica. Two hundred grams of alcohol was passed during 2 hours over this catalyst at 350°. Decomposition was slight; the product consisted of 4 g. of material boiling at 35–50° and about 20 g. boiling at 50–120°, the former being a mixture of aldehyde and amylene. In another experiment, 200 g. of alcohol was passed at the same speed, through an empty copper tube at 540°. Decomposition was very slight, only 2–3 g. of hydrocarbon being produced.

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[1] Corson, Ind. Eng. Chem., Anal. Ed., *6*, 297 (1934).

[2] Pines, J. Am. Chem. Soc., *55*, 3892 (1933).

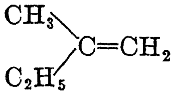
The amount of amyl alcohol decomposed into amylene and water in the presence of alumina depends upon the time of contact and the temperature. Of course, the latter must not be too high, otherwise amylene, itself, decomposes. It is immediately evident when the temperature is too high since an evolution of gas is observed. By choosing a temperature of 500° and an alcohol charging rate of 200 g. per hour, an excellent yield of amylene is obtained and there is no evolution of gas. Data for a number of experiments on the dehydration of isoamyl alcohol are tabulated below.

TABLE 17

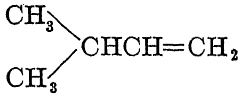
DECOMPOSITION OF ISOAMYL ALCOHOL

AMYL ALCOHOL, PASSED, G.	REACTION T., °C.	TIME, MIN.	AMYLENE OBTAINED, G.	YIELD, % OF ALCOHOL DECOMPOSED	AMYLENE INSOLUBLE IN $H_2SO_4-H_2O$, (2:1) G.
98	345	90	7	10	
393	395–400	170	80	37	30
267	396–400	210	115	38	40
394	440–450	100	110	36	40
395	440–450	120	135	44	35
369	440–450	180	210	68	35
395	498–500	120	200	66	35
400	500–505	180	260	85	40
400	540	130	260	85	40
400	540	250	280	92	48

Amylene obtained from fermentation amyl alcohol by catalytic dehydration over alumina must necessarily consist of two isomers, unsym-methylethylethylene (I) and isopropylethylene (II)



I

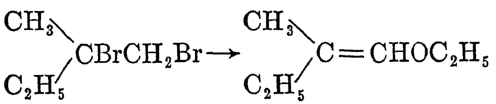


II

since the starting material consists of a mixture of two alcohols, 2-methyl-1-butanol and isobutyl carbinol, as shown by the experiments of Flavitsky, Vishnegradsky, and Eltekov. Experiments confirmed our expectation that the product would be a mixture but we also obtained a third substance namely, trimethylethylene. The product, after drying over calcium chloride, distilled at 26–41°. When treated with sulphuric acid (two volumes of acid to one volume of water) according to the method of Vishnegradsky, a part of the material was insoluble in sulphuric acid and had the boiling point (21–24°) and other properties of isopropylethylene.[1] The relative amount of isopropylethylene varied somewhat in different experiments, as may be seen from the table. This variation will be explained later when catalytic isomerization is discussed.

In order to prove the presence of unsym-methylethylethylene and trimethylethylene, 70 g. of the catalytic product, boiling at 26–41, was diluted with ether and 160 g. of bromine was added to the cold solution. The product (185 g.; boiling point, 70–75° at 20 mm.) was treated with alcoholic potassium hydroxide under a reflux condenser in order to remove the first molecule of hydrogen bromide.

The unsaturated bromide thus obtained (boiling point, 110–130°) was treated with alcoholic potassium hydroxide in sealed tubes at 150° for ten hours. The reaction product consisted chiefly of dimethylallene (boiling point, 40–42°) but there was a small amount of valeric ether (boiling point, 115–120°). Dimethylallene could originate from the bromides of isopropylethylene and trimethylethylene [2] and the valeric ether from the methylethylethylene bromide: [3]



$$\begin{matrix} CH_3\diagdown & & CH_3\diagdown & \\ & CBrCH_2Br \longrightarrow & & C=CHOC_2H_5 \\ C_2H_5\diagup & & C_2H_5\diagup & \end{matrix}$$

The presence of trimethylethylene in the original amylene was proved by the formation of a nitrosochloride (melting point, 72–75°) and a nitrosate (melting point, 95–96°) by the action of nitrosylchloride.

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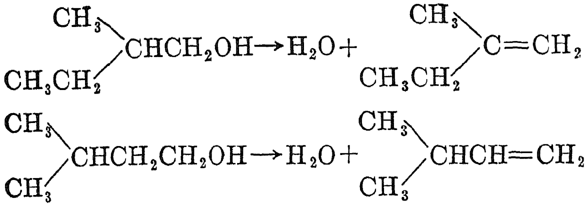
[1] In all probability isopropylethylene was contaminated with another amylene which is insoluble in sulphuric acid.

[2] Favorsky, J. prakt. Chem., (2), *37*, 393 (1888).

[3] Eltekov, J. Russ. Phys. Chem. Soc., *9*, 173 (1877); Ber., *10*, 706 (1877).

Thus, the presence of at least three isomers in the amylene obtained by the catalytic method was proved, although isopropylethylene and methylethylethylene are the normal products of the removal of the elements of water from the corresponding alcohols.



$$\begin{matrix}CH_3\diagdown\\ \quad CHCH_2OH\\ CH_3CH_2\diagup\end{matrix} \rightarrow H_2O + \begin{matrix}CH_3\diagdown\\ \quad C{=}CH_2\\ CH_3CH_2\diagup\end{matrix}$$

$$\begin{matrix}CH_3\diagdown\\ \quad CHCH_2CH_2OH\\ CH_3\diagup\end{matrix} \rightarrow H_2O + \begin{matrix}CH_3\diagdown\\ \quad CHCH{=}CH_2\\ CH_3\diagup\end{matrix}$$

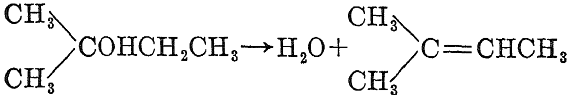
Trimethylethylene is an abnormal product, and is formed by the phenomenon of catalytic isomerization which will be discussed later.

Isopropylethylene, being the chief product of the catalytic dehydration of isoamyl alcohol of fermentation, is, therefore, prepared conveniently by this method.

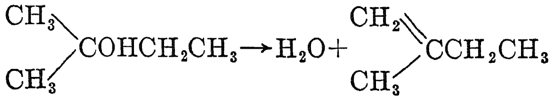
Decomposition of Dimethylethyl Carbinol

When dimethylethyl carbinol is passed through a copper tube containing alumina at 380°, the alcohol is decomposed into amylene and water. Ninety-seven grams of dimethylethyl carbinol passed over the catalyst during 30 minutes produced about 60 g. of amylene (b.p., 35–40°) and 21 g. of water. In another experiment, 198 g. of the carbinol passed at 380–390° in 135 minutes, gave 150 g. of amylene (b.p., 35–40°) and 40 g. of water. In still another experiment 196 g. of alcohol, passed over alumina at 390–400° in 150 minutes, gave 150 g. of a hydrocarbon, which boiled at 35–41°. The evolution of gas was not observed in any of the experiments.

In order to determine the composition of the amylene obtained by the catalytic method, the following experiments were carried out. Twenty-five cubic centimeters of the hydrocarbon was shaken with sulphuric acid (two volumes of acid to one volume of water); or a weaker solution (two parts by weight of sulphuric acid and one part by weight of water) whereupon it dissolved without residue. By the action of nitrosyl chloride, the nitroso chloride (melting point, 72°) characteristic of trimethylethylene was formed. These experiments indicate that the amylene investigated consisted of trimethylethylene, which is a normal dehydration product in the sense that the hydroxyl group of the alcohol combined with a hydrogen atom of the less hydrogenated carbon:

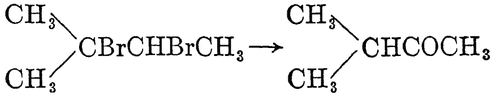


But the removal of water might also occur according to another scheme so as to produce methylethylethylene and experiments actually show that the latter hydrocarbon is also present.

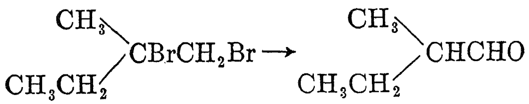


The method of Eltekov was utilized in order to determine whether or not methylethylethylene was present. The amylene was first converted into its bromide which was then heated in a sealed tube with lead oxide and water. The products were methylisopropyl ketone and methylethyl acetaldehyde, the latter being easily separated by oxidation with silver oxide to methylethyl acetic acid. The ketone (I) corresponds to trimethylethylene and the substituted acetaldehyde (II) to methylethylethylene.

(I)



(II)



Decomposition of Trimethyl Carbinol

Trimethyl carbinol, passed over alumina at 420°, decomposes completely into isobutylene and water. This butylene is distinguished by a high degree of purity (99%) and on adding it to an aqueous solution of hydrogen bromide or iodide it gives tertiary butyl bromide which is completely soluble in water on heating.

Since kaolin, and not alumina itself, was present in my first graphite tubes, it was reasonable to expect that kaolin, also, would promote the ethylene decomposition of alcohols. Experiment showed this supposition to be true—kaolin is as effective a catalyst for the production of pure olefins as is alumina. However, the temperature of decomposition is higher than with alumina and for this reason, carbon may be deposited on the contact mass which decreases the activity of the catalyst and also promotes other reactions such as dehydrogenation to aldehyde. Kaolin, however, is an effective catalyst for the production of ethylene from ethyl alcohol, especially if the alcohol contains a certain amount of water.

During the World War, both of these catalysts, kaolin and alumina, were utilized in order to obtain the enormous quantities of ethylene required for the manufacture of mustard gas.

ACTIVITY OF THE ALUMINA CATALYST

From the very beginning of my investigations on the decomposition of alcohol under the influence of alumina, I observed a very important fact,[1] namely, that not every alumina is a good catalyst for the dehydration of alcohol. Some samples of alumina yield a product containing only 50–60% of olefin, the remainder being methane, hydrogen, and carbon monoxide. Moreover, some samples of alumina function at 360–400° whereas others require temperatures of 500–550°. A study of the catalytic activities of various samples of alumina as related to their other properties soon led me to an understanding of the requirements necessary for catalytic activity. Alumina, in order to be an effective dehydration catalyst, must contain a certain minimum amount of water of hydration, perhaps corresponding to the formula $AlO(OH)$. Further discussion of the subject will be found in the chapter on the theory of catalysis.

Thus, when alumina is prepared for catalytic work by precipitation and drying, it must not be heated too strongly (not above 400°) and it must be tested each time for solubility in acid and alkali. To be a good catalyst, alumina must dissolve easily in warm hydrochloric or sulphuric acid and also in concentrated sodium hydroxide solution.

In one of my early papers I described the preparation of active alumina and the method of testing it. Later Senderens[2] and others carried out a series of investigations on the catalytic activity of alumina and aluminum salts in the ethylene-water decomposition of alcohols. Senderens used a Jena glass tube 70 cm. long and 15 mm. in diameter.

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[1] Ipatieff, Ber., *37*, 2986 (1904).

[2] Senderens, Ann. chim., (8), *25*, 449 (1912).

TABLE 18

CATALYST	TEMP. AT WHICH THE REACTION STARTS	VELOCITY OF GAS EVOLUTION, CC./MIN. AT		PERCENTAGE OF ETHYLENE IN THE GAS
		340°	370°	
Aluminum Phosphate	320	9	20	99.5
Aluminum Silicate	270	54	78	99.5
Molding Kaolin	270	52	75	97.8
Aluminum Sulphate, anhydrous	265	75	100	99.5
Precipitated Alumina	250	90	90	99.5

It is seen that these catalysts all give practically pure ethylene but they differ in their effect upon the speed of dehydration.

After my discovery of the catalytic properties of alumina, Sabatier and Mailhe [1] and others carried out experiments on the decomposition of alcohols under the influence of other oxides and found that thorium oxide and blue tungsten oxide are also very good catalysts for this purpose. They concluded that thorium oxide is the best catalyst for the ethylene decomposition of alcohol because, according to their statement, aluminum oxide soon loses its activity.[2] On the other hand, my investigations,[3] the industrial application of alumina for the preparation of ethylene, and the investigations of Engelder [4] indicate that alumina is a very rugged catalyst and because of its cheapness is the best catalyst for commercial dehydration.

In addition to the papers by Sabatier and Mailhe, I would like to call attention to one by Senderens,[5] in which he describes a series of substances such as pumice, calcium phosphate, magnesia, and others, which he claims can be substituted successfully for my alumina catalyst. He also states that red phosphorus is an excellent contact material for the preparation of pure olefins.

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[1] Sabatier and Mailhe, Bull. soc. chim., (4), *1*, 107, 341, 524, 733 (1907).

[2] Sabatier and Mailhe, Ann. chim., (8), *20*, 299 (1910).

[3] Ipatieff, Ber., *34*, 1057 (1902); Ber., *35*, 449 (1903).

[4] Engelder, J. Phys. Chem., *21*, 676 (1917).

[5] Senderens, Compt. rend., 144 (1917).

It is interesting to note here one fact concerning the application of the reaction discovered by me for the preparation of olefins from alcohol by means of alumina. (I did not take out any patents until 1914 on the catalytic processes which I had discovered.) The well-known chemical plant of Schering in Berlin, Germany, immediately after the publication of my paper in 1903 on the preparation of ethylene from ethyl alcohol repeated my experiments with the idea of industrial application. These experiments were unsuccessful and they wrote me a letter asking me to explain the reason for their failure. I saw at once the reasons and wrote them, describing the conditions under which the reaction must be conducted and how the alumina has to be prepared. I received a gratifying letter from Schering and besides this, an entirely unexpected money premium.

Concerning pumice, Nef [1] had already shown that ethyl alcohol was decomposed by contact with this material into olefin, aldehyde, and other substances. I had already tested magnesia and barium oxide and had observed no catalytic decomposition when ethyl alcohol vapor was passed over these substances at 450–500°.

It is true that red phosphorus does decompose alcohols into olefin and water and that the temperature of initial decomposition is somewhat lower than in the case of alumina but the olefin is not pure. For instance, alumina decomposes isobutyl alcohol to yield pure isobutylene whereas red phosphorus gives a mixture of butylenes.

I will describe one experiment on the decomposition of isobutyl alcohol in the presence of red phosphorus. One hundred and forty grams of alcohol was passed, during a period of 95 minutes, through a glass tube containing red phosphorus, heated to 360°; 26.5 liters of gas was evolved, the analysis of which showed 88.2% of olefin and 11.8% of hydrogen and paraffins. The gas was passed into an aqueous solution of hydriodic acid; the resulting iodide distilling at 100–117°. This iodide did not dissolve completely in water even on long heating. The undissolved iodide which boiled at 118–120° could be the iodide formed by the addition of hydrogen iodide to alpha- or beta-butylene.

The temperature of initial decomposition of alcohol in the presence of red phosphorus is not below 250°; and the reaction is scarcely perceptible even at this temperature. The decomposition is more rapid at 330–360°, but in general, it is slower at this temperature than with alumina at 420°. To raise the temperature of the phosphorus above 360° is dangerous; even at 350° there is some distillation of yellow phosphorus.

The catalytic decomposition of alcohol by phosphorus pentoxide had long been known through the researches of Nef who observed the formation of olefins. The application of this reaction to isobutyl alcohol yields a mixture of butylenes.

Alumina was employed not only for the dehydration of aliphatic alcohols but also for cyclic alcohols and since the latter decompose better under pressure, the dehydration of cyclic alcohols will be discussed later.

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[1] Nef, Ann., *318*, 1 (1901).

DEHYDRATION UNDER PRESSURE

To recapitulate, alcohols decompose into olefin and water on passing through a heated copper tube containing alumina, the temperature of practical decomposition being around 400°. However, ethyl alcohol starts to decompose at 320° and the decomposition temperature of a given alcohol depends also on the mode of preparation of the alumina. The experiments on the decomposition of isoamyl alcohol,[1] which were carried out under a variety of conditions of temperature and time of contact, showed that high yields of olefin could be obtained (more than 90% of the theoretical). Therefore, such high yields led me to believe that I was dealing with an irreversible reaction.

But when the dehydration of alcohol was carried out under high pressure in the presence of alumina, three products were observed instead of only two—ethylene, water, and ethyl ether. Pressure diminishes the decomposition of the alcohol into ethylene and forces it in the direction of ether.

$$2C_2H_5OH \rightleftharpoons C_2H_5OC_2H_5 + H_2O$$

It was found that the formation of ethers is characteristic of all primary and secondary alcohols when subjected to the catalytic influence of alumina and that this reaction is *reversible.* This decomposition of alcohol into ether and water takes place at temperatures above the critical and, therefore, represents a typical case of the dissociation of a gaseous body by the catalytic effect of a solid surface, this sort of heterogeneous catalysis being very interesting from the point of view of chemical mechanics. There are very few such reversible catalytic reactions known among organic compounds. Konovalov [2] observed the catalytic decomposition of complex ethers at temperatures employed in the determination of their vapor density, and found the reaction to be reversible. In these investigations it was established that many solid bodies not acting chemically upon the given ether promoted decomposition, and that the velocity of this contact decomposition increased with a diminution of the pressure to a certain limit, after which it became constant. I did not study the decomposition of complex ethers at high pressures under the influence of various catalysts, and therefore, have no data on the cause of this catalytic decomposition. The dissociation of alcohol into ether and its reverse reaction in the presence of alumina is based on the ability of alumina to react with water. The presence of alumina lowers the temperature of this decomposition. The appearance of ether as one of the products is interesting from the point of view of intermediate compound formation.

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[1] Ipatieff, J. Russ. Phys. Chem. Soc., *35*, 577 (1903).

[2] Konovalov, J. Russ. Phys. Chem. Soc., *17*, 373 (1885).

If these high pressure experiments had not been made, it is doubtful if I would have ever realized that ether was a primary product of the dehydration of alcohol over alumina. However, after finding ether in the high pressure experiments, the products of dehydration at ordinary pressure were carefully scrutinized [1] and ether was found to be present, but only in small amount.

Below, I will mention a number of experiments on the decomposition of ethyl alcohol and of ether (both at ordinary and at high pressure) so as to bring out certain characteristics of alumina as well as the influence of temperature.

Ethyl Alcohol

As already mentioned, any sample of alumina is not necessarily a good catalyst. Experiment 241 (see Table 19), shows that alumina which has been strongly ignited and which is, therefore, insoluble in sodium hydroxide and hydrochloric acid required a much higher temperature in order to dehydrate alcohol, than did alumina which had not been ignited, and which was, therefore, soluble in these two reagents. It is also to be noticed that the ignited alumina produced a certain amount of hydrogen and butadiene-1, 3 besides ethylene and water. This type of decomposition will be discussed later in a special chapter.

Most of the experiments on the decomposition of ethyl alcohol under high pressure were made in the high pressure apparatus described above in which a copper tube was placed inside of the iron tube. However, a few experiments were made in an iron tube, since, up to a certain temperature, iron is not a catalyst and does not interfere with the action of the alumina.

Thirty-eight grams of alcohol and 2 to 3 g. of alumina were used in each experiment, the tube being heated in an electric furnace as previously described. In Table 19, there are listed three series of experiments which were made at ordinary and at high pressure, sometimes the tube being iron and sometimes copper. For certain of the experiments, curves were constructed showing the relationship of pressure increase as a function of time, making possible the determination of dp/dt and the constant K.

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[1] Ipatieff, Ber., 37, 2986 (1904).

In the first series of experiments on decomposition at ordinary pressure, ethyl ether was formed, but it was only at the lower temperatures that significant amounts could be isolated. Alumina promotes pure ethylene decomposition in iron at temperatures up to 450–460°; above this temperature, iron begins to function catalytically, promoting aldehyde decomposition, and at 520°, according to the gas analyses, the ethylene and the aldehyde decomposition are about equal. Experiment 241 demonstrates that the stronger the alumina is ignited, the less pure is the ethylene obtained. With ignited alumina, formation of divinyl is observed which very likely results from the decomposition of ethyl ether with accompanying liberation of water and hydrogen.

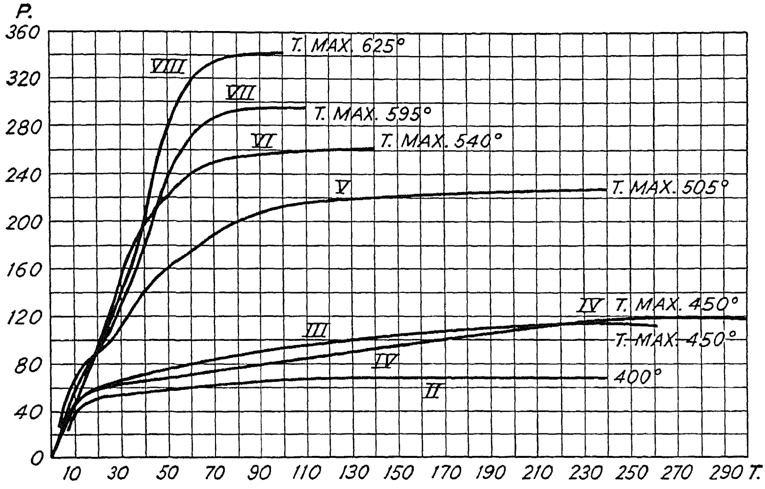

FIG. 9

The second series of experiments on the decomposition of ethyl alcohol (at high pressure, in a copper tube, in the presence of alumina) shows that ether is the chief product when the heating period is short and the temperature is not above 490° (Expt. 245).

TABLE 19

EXPT. No.	TIME, MIN.	T., °C.	p, ATMS.	p, FINAL ATMS.	CATALYST	ANALYSIS OF GAS IN %					AMOUNT OF GAS IN LITERS
						C_nH_{2n}	CO_2	CO	H_2	C_nH_{2n+2}	
241	45	425	1		Al_2O_3 heated	73.0			27.0		16.5
243	40	385	1		Al_2O_3	98.4			1.6		13.5
244	30	520	1		Clay	97.3			2.7		13.0
271	50	360	1		Al_2O_3	98.0			2.0		12.5
291	45	380	1		Al_2O_3	98.0			2.0		12.6
293	60	500	1		Al_2O_3 + Cu	95.0			5.0		21.7
297	60	520	1		Al_2O_3 + Cu	96.0	0.0			4.0	27.2
298	60	530	1		Al_2O_3 + Fe	52.0	0.4	2.0	34.9	10.6	38.6
257	120	525	High pressure		Al_2O_3 + Cu	15.6	3.2	7.6	46.4	26.9	4.1
245	50	490			Alumina and copper "	Ethylene					0.2
251	15	510			"	96.0					2.0
249	20	530			"	95.2			1.6	1.0	3.6
301	420	505			"	13.0	4.6	9.6	13.8	59.2	5.0
302	180	520			"	3.2	3.2	12.6	10.8	59.6	5.5
304	180	530			"	10.8	5.2	12.8	16.2	55.2	7.5
319	130	530	170	24	"	14.6	4.0	14.2	12.4	54.6	5.5
305	180	540	High pressure		"	10.6	3.2	13.3	11.6	60.8	7.7
306	20	560			"	55.8	0.8	5.6	8.9	27.8	4.5
308	180	560			"	9.6	7.1	10.8	8.5	63.6	15.2
296	60	615			"	4.2	6.2	8.8	6.8	74.8	19.2
321	255	530	208	27	"	12.6	3.2	14.6	10.4	58.8	5.8
324	60	530	185	19	"	78.4	0.2	1.6	7.6	11.8	3.7
325	90	570	235	22	"	33.8	1.8	12.6	2.0		4.9

TABLE 19 (*Continued*)

EXPT. No.	TIME, MIN.	T., °C.	p, ATMS.	p, FINAL ATMS.	CATALYST	ANALYSIS OF GAS IN %					AMOUNT OF GAS IN LITERS
						C_nH_{2n}	CO_2	CO	H_2	C_nH_{2n+2}	
316	240	400	70		Al_2O_3 + Fe						0.0
317	210	450	118		Alumina and iron	Ethylene					3.6
312	210	500	231			9.6	7.2	11.6	13.8		14.0
334	140	540	260			9.2	4.4	8.8	11.4		16.2
349	70	595	290			6.6	5.0	4.2	11.6		18.5
300	60	620	High press.			8.0	6.8	2.4	7.4		20.6
314	40	625	343	69		1.8	6.8	4.1	8.2		22.7
294	50	550	High press.			9.6	5.3	12.4	8.6		8.0

With a still shorter period of heating and a higher temperature, both ether and ethylene are found in addition to water (Expt. 249). At temperatures above 500° and with long heating, other products appear in the gas; the higher the temperature and the longer the heating, the poorer the gas is in olefin and the richer in saturated hydrocarbons. The duration of heating plays an important part. When ethyl alcohol was heated 4 hours at 530° (Expt. 321), the gas contained 12% of ethylene; when the heating period was only 1 hour at the same temperature (Expt. 324), the gas was 78% ethylene. Likewise, at 560–570° (Expts. 306 and 325) the yield of ethylene was considerably greater with short heating than with long heating.

In the third series of experiments on the high pressure decomposition of alcohol in the presence of alumina, the reaction vessel was iron. Experiment 316 (Curve II) was made at 400° and the sole products of the reaction were ethyl ether and water: the system, alcohol, ether, and water, adjusted itself at the equilibrium value corresponding to the dissociation pressure of alcohol at that temperature.

$$2C_2H_5OH \rightleftarrows H_2O + C_2H_5OC_2H_5$$

When the pressure is now increased, the ether decomposes into ethylene and water according to the following equation:

$$C_2H_5OC_2H_5 \rightleftarrows H_2O + C_2H_4$$

and as shown in Experiment 370 (Curves III and IV), the pressure curve becomes parallel to the abscissa after a certain time interval at 450°, which indicates that in the system alcohol, ether, water, and ethylene a state of equilibrium has been reached. Unfortunately, insufficient work has been done on these interesting equilibria for a complete understanding.

In any case, these experiments indicate the importance of pressure. Whereas at ordinary pressure, alcohol begins to decompose into ethylene and water at 350°, at 400° under high pressure, the only products of decomposition are diethyl ether and water.

At 530° (see curves for Expts. 319 and 321) we also observed [1] that the pressure rose to a maximum above which it did not increase in spite of the fact that a certain amount of alcohol remained unchanged, which indicated that equilibrium had been attained. At still higher temperatures the character of the decomposition was similar to that obtained in the presence of iron. This result is understandable for those experiments made in iron tubes and it should be mentioned that there was also a chance of alcohol coming in contact with iron surfaces even in those experiments in which the iron pressure vessel was lined with a copper tube since the end of the copper tube was not sealed to the iron. In all experiments made at temperatures higher than 520° there was always a small amount of carbonaceous residue, the quantity increasing with rise in temperature. At 620°, the only products were carbon, water, and heavy condensation products.

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[1] The difference in pressures in these two experiments might be explained by the fact that in Experiment 319, 33 g. of alcohol was taken which was 5 g. less than in Experiment 321.

At 530°, the yield of ether was about 30% of the theoretical amount corresponding to the alcohol taken; at lower temperatures the yield of ether was greater.

At temperatures above 520°, an additional product was observed in very small amount—an unsaturated material similar to that obtained in the decomposition of ethyl alcohol in the presence of iron. (See further.)

In order to appreciate the change in the speed of decomposition of ethyl alcohol in the presence of alumina, curves were plotted with pressure as a function of time. Tables and Curves IX, X, XI, and XII show the course of decomposition in a copper tube in the presence of alumina, whereas Tables and Curves III, V, VI, VII, and VIII depict the course of reaction in an iron tube in the presence of alumina.

The maximum velocity of pressure increase for Curve IX, $(dp/dt)_{\max}$, is proportional to the velocity of decomposition and it was found to be $21/5 = 4.2$. The time required for development of the maximum pressure at 530° was 105 minutes and, therefore,

$$\left(\frac{dp}{dt}\right)_{\max} \cdot t = K = 441 \text{ k.m.}^1$$

For Curve X, $(dp/dt)_{\max} = 15/5 = 3$ and the time 135 minutes. The value K calculates to be 415 k.m.

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[1] k.m. is abbreviation for kilograms × minutes.

For Curve XI, $(dp/dt)_{\max} = 32/5 = 6.4$ kilos; for Curve XII, $(dp/dt)_{\max} = 25/5 = 5$ kilos. If the reaction represented by Curve XI had been carried to completion we would have found the value K as we did for Curves IX and X; for Curve XII, the value K would be slightly larger.

TABLE 20

Table IX, Curve IX			*Table X, Curve X*			*Table XI, Curve XI*		
TIME, MIN.	T., ° C.	p, ATMS.	TIME, MIN.	T., ° C.	p, ATMS.	TIME, MIN.	T., ° C.	p, ATMS.
0	320	17	0	315	14	0	310	12
10	380	49	10	375	46	10	380	46
20	415	61	20	410	62	20	425	69
40	460	80	30	420	71	30	455	81
55	490	100	50	440	81	35	475	100
60	500	114	60	460	97	40	490	110
65	520	135	70	480	116	45	500	125
70	515	150	75	485	130	50	510	157
75	525	154	80	502	145	55	520	170
105	530	159	85	515	160	60	535	185
145	535	162	90	575	171			
175	535	168	124	530	201			
195	535	170	155	530	204			
205	535	170	215	530	204			

Table XII, Curve XII			*Table III, Curve III*			*Table V, Curve V*		
TIME, MIN.	T., ° C.	p, ATMS.	TIME, MIN.	T., ° C.	p, ATMS.	TIME, MIN.	T., ° C.	p, ATMS.
0	330	16	0	350	39	0	360	30
10	365	36	10	365	51	10	410	67
20	410	61	20	380	56	20	435	87
30	435	75	30	400	60	30	462	110
40	460	90	40	400	61	35	478	123
50	485	105	50	400	64	40	485	139
55	495	118	60	415	68	45	500	152
60	505	131	70	428	72	55	505	169
65	515	151	80	432	77	65	505	183
70	525	168	90	430	80	75	505	197
75	535	186	120	445	88	85	500	293
80	545	209	150	448	97	105	505	212
85	557	223	180	450	104	115	505	216
90	570	235	210	450	112	125	505	220
			270	450	118	135	505	221
			300	450	118	245	505	221

TABLE 20 (*Continued*)

Table VI, Curve VI			*Table VII, Curve VII*			*Table VIII, Curve VIII*		
TIME, MIN.	T., °C.	p, ATMS.	TIME, MIN.	T., °C.	p, ATMS.	TIME, MIN.	T., °C.	p, ATMS.
0	380	30	0	390	14	0	330	15
10	450	80	10	430	50	10	390	60
20	480	99	20	480	82	20	440	90
25	510	123	30	520	122	30	495	130
35	530	153	40	560	180	35	520	155
40	535	172	45	575	228	40	540	188
45	540	197	50	580	248	45	560	248
50	535	212	60	590	276	50	575	280
55	540	235	70	595	289	55	590	303
60	535	240	89	595	290	60	600	329
70	535	245	90	595	290	65	610	332
80	535	249	91	595	290	70	625	340
100	540	257	92	595	290	75	625	342
124	538	259	93	595	294	85	625	345
130	540	260	96	595	290			
130	540	260	99	595	290			

Thus, we see, that the expression $(dp/dt)_{\max} \cdot t$, corresponding to the decomposition of alcohol in the presence of alumina, is a constant up to a certain temperature and has the value of about 400 k.m.

Consideration of Curve III leads to the conclusion that the decomposition of ethyl alcohol with the formation of ethylene proceeds very slowly and approaches a certain limit, $(dp/dt)_{\max}$ being $5/10 = 0.5$.

For the decomposition of alcohol at 505°, represented by Curve V, $(dp/dt)_{\max} = 16/5 = 3.2$. Curve V shows that after 130 minutes of heating, the pressure increases very slowly. If the time required for attainment of maximum pressure is characteristic for the catalytic decomposition of alcohol in the presence of alumina, then the constant K should be 416. But at this temperature, the presence of iron promotes a further decomposition and after 245 minutes of heating, the value of K was found to be 784 k.m.

CURVE No.	$(dp/dt)_{\max}$	t, MIN.	K
VI	$30/5 = 6$	130	780 k.m.
VII	$48/5 = 9.6$	80	768 k.m.
VIII	$60/5 = 12$	70	840 k.m.

Thus, up to 500° the constant K corresponding to the decomposition of ethyl ether in the presence of alumina, both in copper and iron tubes, has the value of about 400 k.m. Above this temperature, K increases to 800 k.m.; in other words, at high temperature the catalytic effect of alumina on alcohol is similar to that of iron, not only as regards the rate of reaction but also the nature of the gaseous products.

Ethyl Ether

The decomposition of ether was studied at ordinary and superatmospheric pressure in the presence of alumina and also iron catalysts. The data are summarized in Table 21.

The first series of experiments was run at ordinary pressure, 100 g. of ether being charged each time. In the absence of catalyst, ether does not decompose until the temperature of 580° has been reached (Expt. 279), whereas in the presence of alumina in a copper tube, ether starts to decompose at 330° with abundant formation of pure ethylene and water. There was a certain amount of unchanged ether and also some alcohol (5–9 g.). The presence of the latter proves that ether is hydrated to alcohol through the aid of alumina, in other words, that at high temperature dehydration of alcohol is reversible.

Ether vapor, passed through an iron tube, starts to decompose at 520° and at 570° there is rapid decomposition, the chief product being acetaldehyde (Expt. 284). Since ether is in equilibrium with alcohol, the formation of aldehyde is the normal decomposition product of alcohol in the presence of iron at high temperature. When 38 g. of ethyl ether was heated in the high pressure apparatus in a copper tube without a catalyst, decomposition occurred above 490°. In the presence of catalytic alumina, decomposition starts at 400° and proceeds rapidly at 450°, with production of ethylene and ethyl alcohol, and it should be realized that alcohol is formed from ether whether the original ether is wet or dry. Only a small amount of ethylene is formed when an equimolecular mixture of ether and water is heated, even above 450°; in other words, the presence of water inhibits the decomposition of ether. At higher temperatures and with longer heating, ether decomposes into a variety of gaseous products, the chief component, however, being ethylene. When the heating period is brief (Expt. 272), the product is mostly ethylene. When ether is decomposed in the presence of alumina under high pressure, a small amount of carbon is always deposited, as is also true in the decomposition of alcohol

TABLE 21
ETHYL ETHER

EXPT. No.	TIME, MIN.	T., °C.	p, ATMS.	p, FINAL ATMS.	CATALYST	ANALYSIS OF GAS IN %					AMT. OF GAS, LITERS	PRODUCTS
						C_nH_{2n}	CO_2	CO	H_2	C_nH_{2n+2}		
279	80	580	Atm.		No catalyst						4.0	Aldehyde and alc.
281	60	530			Cu + Al_2O_3	Ethylene					13.2	6 g. Ethyl alcohol
275	30	510			Cu + Al_2O_3	"					22.2	
287	90	360			Cu + Al_2O_3	"					18.0	9 g. Ethyl alcohol
289	75	360			Cu + Al_2O_3	"					19.0	7 g. Ethyl alcohol
282	70	520			Fe						4.0	Traces of aldehyde
284	65	570			Fe	11.8	0.4	11.2	23.6	46.8	11.3	Aldehyde

TABLE 22
ETHYL ETHER (*Continued*)

	EXPT. No.	TIME, MIN.	T., °C.	p, ATMS.	p, FINAL ATMS.	CATALYST	ANALYSIS OF GAS IN %					AMT. OF GAS, LITERS	PRODUCTS
							C_nH_{2n}	CO_2	CO	H_2	C_nH_{2n+2}		
	265	240	420	> Atm.		Cu (tube)							
	272	40	560	> Atm.		Cu (tube) + Al_2O_3	41.4	2.0	7.4	12.2	36.2	4.4	Ald. and cond. products
		180	515	> Atm.		Cu (tube) + Al_2O_3	22.2	3.4	13.2	11.4	48.6	3.6	
Series II	277	45	515	150	19	Cu (tube) + Al_2O_3						4.1	
	280	180	490	> Atm.		Cu without catalyst	5.8	3.6	7.0	11.6	71.4	1.4	Traces of ald.
	283	300	490	120	21	Cu without catalyst							
	353	300	400	56		Cu + Al_2O_3	Ethylene					0.1	
	354	230	450	112	16	Cu + Al_2O_3	Ethylene					5.5	
	373	225	545	282	60	Cu + Al_2O_3	2.6	5.2	17.0	7.0	67.6	17.25	8 g. Liquid
	288	300	480	78		Fe + Al_2O_3	2					0.1	

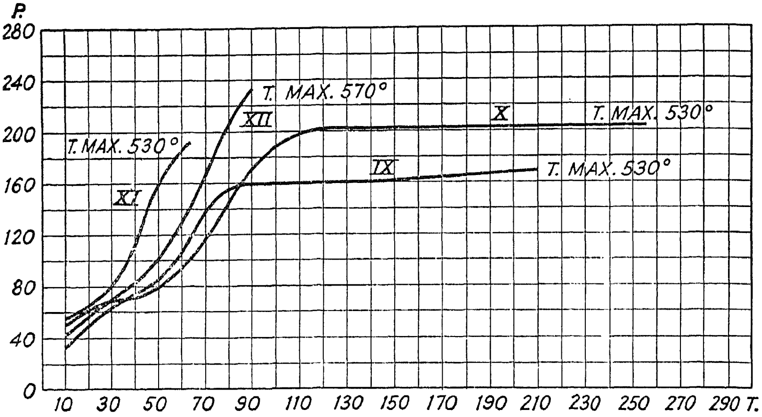
P.
280
240
200
160
120
80
40
0
10
30
50
70
90
110
130
150
170
190
210
230
250
270
290
T.
T. MAX. 570°
XII
X
T. MAX. 530°
T. MAX. 530°
XI
IX
T. MAX. 530°

Fig. 10

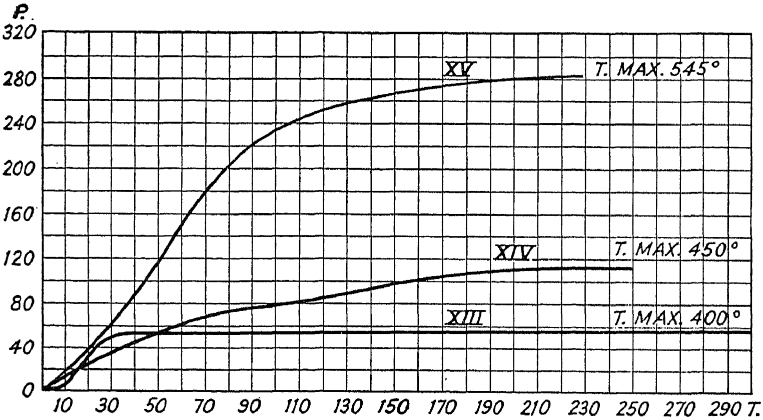
P.
320
280
240
200
160
120
80
40
0
10
30
50
70
90
110
130
150
170
190
210
230
250
270
290
T.
XV
T. MAX. 545°
XIV
T. MAX. 450°
XIII
T. MAX. 400°

Fig. 11

It is possible that the ether molecule splits at high temperature in the following manner:

$$C_2H_5OC_2H_5 \rightarrow C_2H_4 + CH_4 + H_2O + C$$

And that carbon and water may give the following reactions:

$$C + H_2O \rightleftarrows CO + H_2$$

$$C_2H_5OC_2H_5 + H_2O \rightleftarrows 2C_2H_5OH$$

These last two reactions are reversible and they may define the equilibrium observed in the catalytic decomposition of ether in the presence of alumina and, besides this, they explain also the composition of the gas which is obtained by the decomposition of ether.

Among the liquid products of the decomposition of ether a substance of unsaturated character is found, which is similar to a substance obtained in the decomposition of alcohol in the presence of alumina under high pressure. (This unsaturated substance consists of polymers [1] of ethylene.)

The decomposition of ethyl ether can be seen from the following tables and curves (XIII, XIV, and XII).

TABLE 23

Table XIII, Curve XIII			*Table XIV, Curve XIV*			*Table XII, Curve XII*		
Time, Min.	T., °C.	p, Atms.	Time, Min.	T., °C.	p, Atms.	Time, Min.	T., °C.	p, Atms.
0	300	10	0		8	0	330	18
10	380	35	30	380	45	10	380	39
20	390	48	40	415	54	20	435	60
30	400	51	50	435	62	30	475	80
40	400	52	60	443	67	40	520	113
50	400	54	70	451	70	45	530	136
60	400	56	90	482	77	50	545	158
120	400	56	110	453	87	60	555	182
300	400	56	140	450	98	70	550	207
“	“	“	170	450	106	90	545	232
“	“	“	200	450	112	110	540	230
“	“	“	250	450	112	140	542	261
“	“	“	250	450	112	180	545	271
“	“	“	250	450	112	225	545	282

It is evident that up to 450°, the decomposition of ether in the presence of alumina and under high pressure is similar to that of ethyl alcohol under like conditions.

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[1] Ipatieff, J. Russ. Phys. Chem. Soc., *38*, 63 (1906).

At 545° the decomposition of ethyl ether approximates the decomposition of alcohol at the same temperature in an iron tube in the presence of catalytic iron; $(dp/dt)_{\max} = 23/5 = 4.6$ and the time t when $p_{\max}$ is reached in the present case may be considered equal to 180 minutes and therefore, the constant K equals 828. Consequently, with ethyl ether there are two kinds of decomposition which occur, and the same is true for ethyl alcohol.

Normal Propyl Alcohol

Propyl alcohol decomposes under high pressure in a copper tube in the presence of alumina in the same way as ethanol. From 39 g. of alcohol (Expt. 368), heated at 400°, 25 g. of the product was pure propylene. The liquid distilled at 60–100° and consisted of undecomposed alcohol, propyl ether, water, and a small amount of condensation products.

The shape of the pressure curve for propyl alcohol (Curve and Table XVI) and the value $(dp/dt)_{\max} = 8/10 = 0.8$ for the temperature 400°, are similar to those for ethanol.

TABLE 24

Table XVI, Curve XVI

Time, Min.	T., °C.	p, Atms.
0	290	
10	330	10
20	355	25
30	380	42
40	394	50
50	394	54
60	394	58
75	390	61
135	390	68
195	390	81
250	390	89

Here also, there is first the dehydration of two molecules of alcohol to give water and propyl ether,

$$2C_3H_7OH \rightarrow H_2O + C_3H_7OC_3H_7$$

and then the latter decomposes into propylene and water.

Isoamyl Alcohol

Isoamyl alcohol (boiling point, 129–130°), when heated with alumina in the high pressure apparatus in a copper tube, decomposes, first forming isoamyl ether, which in turn splits into water and amylene. It must be noted that the stability of ethers decreases with increase of molecular weight; whereas ethyl ether is formed exclusively from ethanol at 400°, for propyl and especially isoamyl alcohol there is considerable olefin obtained at 400°.

The products of the reaction as well as the course of decomposition are illustrated in the following tables and curves (XVII, XVIII, XIX), page 94.

It is to be noted that the pressure curves become parallel to the abscissa (Curve XIX), which shows that the reaction is reversible. Curve XVIII changes in slope after two and a half hours due to the fact that the temperature, after holding constant at 470° for a while, suddenly rose to 520°. (This was the first run with a new electric furnace and the operation of the equipment was not understood.)

For Curve XVII, $(dp/dt)_{\max} = 7/10 = 0.7$; and
for Curve XVIII, $(dp/dt)_{\max} = 14/5 = 2.8K$.

If we count the time during which $p_{\max}$ was reached as 170 minutes, then $K = (dp/dt)_{\max} \cdot t = 476$ k.m. For the Curve XIX, $(dp/dt)_{\max} = 23/5 = 4.6$, and $t = 90$; $K = 414$ k.m.

Thus, the course of decomposition of amyl alcohol up to the temperature of 550° is very similar to that of ethanol in the presence of alumina.

Isoamyl Ether

When isoamyl ether is passed through a copper tube containing alumina, it decomposes at 400–450° into water and amylene.

$$C_5H_{11}OC_5H_{11} \rightarrow H_2O + 2C_5H_{10}$$

Thus, the decomposition of isoamyl ether proceeds in exactly the same way as that of ethyl ether.

When isoamyl ether is heated in the high pressure apparatus at 400° in the presence of alumina for twelve hours, it decomposes also into amylene and water; the pressure rises to a limiting value within seven hours and remains constant during the last four hours. About 13 g. of hydrocarbon was obtained; a part of the amyl ether was converted into alcohol, and a part of the ether remained unchanged. The hydration of ether into alcohol was brought about

TABLE 25

ISOAMYL ALCOHOL

EXPT. NO.	TIME, MIN.	T., °C.	p, ATMS.	p, FINAL ATMS.	CATALYST	ANALYSIS OF GAS IN %						AMT. OF GAS, L.	AMT. OF LIQUID, G.
						C_nH_{2n}	CO_2	O_2	CO	H_2	C_nH_{2n+2}		
345 Curve XVII	290	400	54		Cu tube Al_2O_3		Amylene		Amyl ether				33
347 Curve XVIII	180	520	138		" " "		"		"	"		0.75	33
348 Curve XIX	75	555	144	12	" " "	4.8	8.48	1.8			65	2.50	24

ISOAMYL ALCOHOL

No. 345, Curve XVII			*No. 347, Curve XVIII*			*No. 348, Curve XIX*		
TIME, MIN.	T., °C.	p, ATMS.	TIME, MIN.	T., °C.	p, ATMS.	TIME, MIN.	T., °C.	p, ATMS.
0	280	6	0	300	10	0	310	6
20	350	15	20	370	23	10	350	12
50	390	23	30	390	33	20	430	32
60	400	30	60	425	58	30	460	49
90	399	38	90	450	100	40	490	79
120	406	46	100	457	106	45	505	102
150	396	49	110	463	110	50	515	117
180	400	53	120	460	111	60	535	131
240	400	54	130	477	114	70	547	136
290	400	54	140	500	118	80	555	140
			145	520	132	90	550	141
			170	525	188	140	550	141
			180	523	187	150	550	141

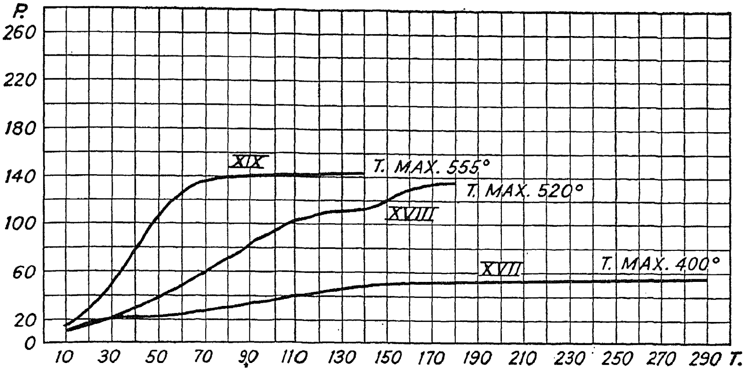

FIG. 12

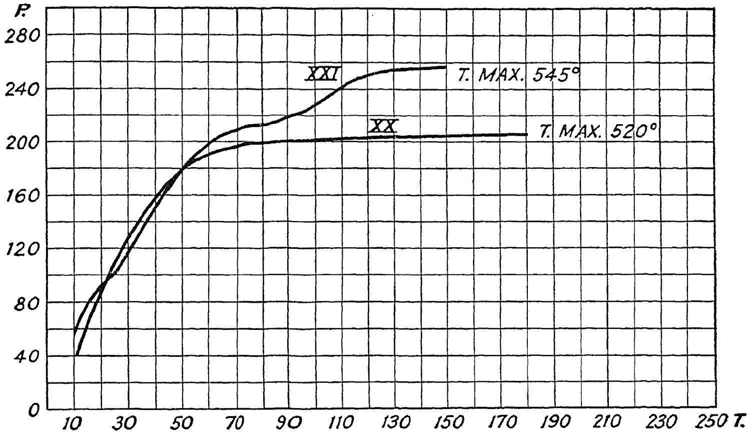

FIG. 13

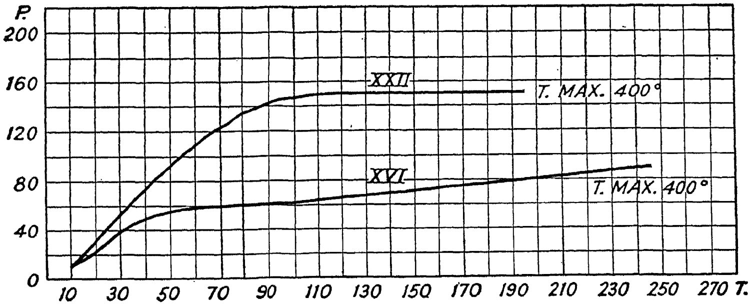

FIG. 14

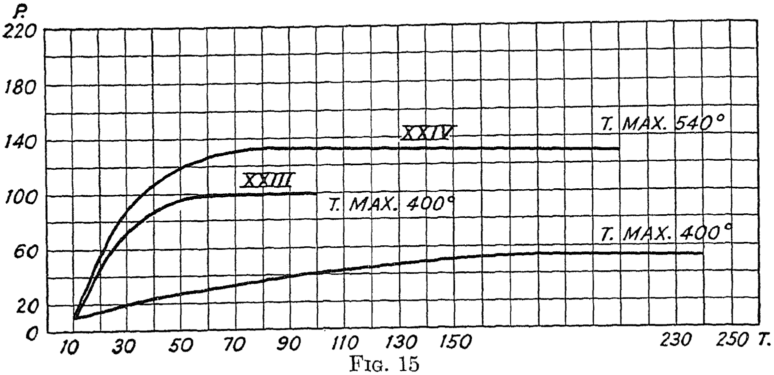

FIG. 15

by the water removed from the ether through the catalytic influence of alumina.

Exactly the same result is obtained when amyl alcohol is treated under the same conditions; 13 g. of amylene is obtained and there is a certain amount of unchanged alcohol. Thus, under the influence of alumina the dissociation of amyl alcohol and of amyl ether proceed in the same manner as that of ethyl alcohol and of ethyl ether.

In order to investigate the effect of water upon the course of the catalytic reaction, an experiment was carried out in which 6 g. of water was added to the initial amyl alcohol. The experimental conditions were the same as in the preceding experiments and the reaction products were also the same; 12 g. of amylene was obtained. Thus, the presence of water in considerable amount does not change the course of the catalysis, and does not prevent the first step of the alcohol decomposition, viz., the formation of ether.

It is interesting to note that the amylene which is obtained under high pressure contains the same isomers as the amylene prepared at ordinary pressure by the dehydration of the alcohol or ether. However, isopropylethylene can be isomerized into trimethylethylene at 480° under high pressure in the presence of alumina as will be discussed later. The hydrocarbon obtained by heating isopropylethylene with alumina in the high pressure apparatus boiled at 25–41° and gave the characteristic nitrosate of trimethylethylene; a portion of the hydrocarbon was soluble in sulphuric acid. The greater part of the amylene, however, polymerized to diamylene under these conditions.

Methanol

Two experiments were made on the decomposition of methanol, one at 520° and the other at 545°. The decomposition of methanol was found to be similar to that of ethanol. First *methyl ether* is formed, which in turn is further decomposed, but not to give any unsaturated hydrocarbon, not even a trace. The formation of methyl ether from methanol represents in itself a reversible reaction,

$$2CH_3OH \rightleftarrows H_2O + CH_3OCH_3$$

and since methyl ether is a gas capable of absorption by sulphuric acid, it is possible to study this reaction from a kinetic point of view. The data on the decomposition of methanol are tabulated below and the course of the decomposition is shown by the Tables and Curves XX and XXI.

The formation of methane, carbon monoxide, and hydrogen might be explained by the decomposition of aldehyde, which was formed from methanol,

$$CH_3OH \rightarrow H_2 + HCHO \rightarrow CO + H_2 + H_2;$$
$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

or these gases may be the decomposition products of methyl ether:

$$CH_3OCH_3 \rightarrow CH_4 + CO + H_2 \rightarrow CH_4 + H_2O + C;$$
$$CH_4 + H_2O \rightleftarrows CO + 3H_2$$

The latter equation of decomposition explains the origin of the carbon, which is always formed and also shows why the reactions should have a limit. For both experiments, $(dp/dt)_{\max} = 20/5 = 4$ and the maximum velocity of decomposition of methyl alcohol is about the same as that of other primary alcohols. But the decomposition temperature of methanol, both with alumina and also with iron, is lower than that for other alcohols. In Curve XX, $K = (dp/dt)_{\max} \cdot 100 = 400$ k.m. and for the other curve (XXI, temperature 545°) the constant K is about 600 k.m., which indicates that the decomposition of methyl ether takes place to a considerable extent.

Isopropyl Alcohol

Isopropyl alcohol was chosen for the study of the decomposition of a secondary alcohol, 38 g. being heated in the high pressure

TABLE 26

METHYL ALCOHOL DECOMPOSITION

EXPT. No.	TIME, MIN.	T., °C.	p, ATMS.	p, FINAL ATMS.	CATALYST	ANALYSIS OF GAS IN %						AMT. OF GAS, L.	AMT. OF LIQUID, G.
						C_nH_{2n}	CO_2	O_2	CO	H_2	C_nH_{2n+2}		
362	180	520	207	10	$CuAl_2O_3$		2.7	1.0	22.4	21.1	51.5	1.6	11.5 Methyl ether
363	150	545	258	52	"		6.6	1.2	11.8	33.0	47.8	9.5	10.0 Methyl ether

TABLE 27

Table XX, Curve XX			*Table XX, Curve XXI*		
TIME, MIN.	T., °C.	p, ATMS.	TIME, MIN.	T., °C.	p, ATMS.
0	320	10	0	370	
10	370	37	10	430	50
20	410	86	20	460	89
30	455	125	30	495	120
35	480	145	35	512	138
40	500	162	40	534	159
50	517	185	50	545	186
65	519	197	70	540	208
85	520	200	90	547	221
100	520	204	110	544	246
160	520	207	130	540	254
185	519	207	150	540	258

apparatus with alumina at 400° for 190 minutes. After cooling (the pressure was 8 atms.), 9.3 liters of gas and 10 g. of liquid were collected, the latter consisting of two layers. Distillation of the liquid showed that it consisted of undecomposed alcohol, isopropyl ether, and some unsaturated material which adds bromine and decolorizes potassium permanganate. The gas was pure propylene; of 100 cc., 97 cc. were adsorbed by bromine. The course of decomposition is illustrated in the following table and curve (XXII).

TABLE 28

Table XXII, Curve XXII

TIME, MIN.	T., ° C.	p, ATMS.
0	250	
25	340	41
35	385	64
40	405	76
50	380	88
70	392	127
80	394	138
90	393	142
100	398	149
105	400	150
190	400	150

The maximum velocity of pressure increase, $(dp/dt)_{\max} = 12/5 = 2.4$, and the product of this value and the time corresponding to the attainment of $p_{\max}$, gives the value 252.3 which is considerably smaller than for primary alcohols.

Comparing the values of $(dp/dt)_{\max}$ for secondary alcohols and primary alcohols, we see that the velocity of decomposition of secondary alcohols is much greater than that for the primary alcohols.

Dimethylethyl Carbinol

For the investigation of the decomposition of a tertiary alcohol under high pressures, dimethylethyl carbinol was chosen, the alcohol being heated at 400 and 540° in a copper tube in the high pressure apparatus with 3 g. of alumina. When the vapors of dimethylethyl carbinol are passed through a copper tube packed with alumina, it decomposes into amylene and water at 260°; that is, its temperature of decomposition is considerably lower than that of primary alcohols. The course of decomposition and the analysis of gaseous products is given in Tables and Curves XXIII and XXIV.

The liquid obtained by the decomposition of dimethylethyl carbinol at 400° consists of amylene boiling at 25–40°, a small amount of condensation products, and water; the tertiary alcohol decomposes directly into amylene and water and the reaction goes to completion. At 540° this tertiary alcohol also decomposes into amylene and water, but a part of the amylene decomposes further at this temperature, whereby saturated hydrocarbons are produced, chiefly methane and ethane. Besides this, amylene also undergoes polymerization as shown by the isolation of a liquid boiling at 100–102° and containing a double bond. The nature of this product has not been clarified.

For Curve XXIII, $(dp/dt)_{\max} = 24/5 = 4.8$ and t corresponding to $p_{\max}$ being 60 minutes, we obtain for K the value 288 k.m.

For Curve XXIV, $(dp/dt)_{\max} = 26/5 = 5.2$, and $t = 60$ minutes, and the product $K = 312$ k.m.

Thus, for tertiary alcohols as well as for secondary, the value of K is much smaller than for primary alcohols; and the maximum velocity of decomposition of tertiary alcohols is much greater than for secondary alcohols. Unfortunately, I studied only one tertiary alcohol and, therefore, do not know whether the value of K is the same for other tertiary alcohols.

Our observations on the catalytic decomposition of alcohols under high pressure lead to the conclusion that the decompositions of the three classes of alcohols differ only in degree—at 400° the value $(dp/dt)_{\max}$ for primary alcohols averages 0.6; for secondary alcohols, 2.4; for tertiary alcohols, 4.8. In other words, the maximum decomposition velocity for primary, secondary, and tertiary alcohols is in the ratio of 1, 4, 8. There is another interesting characteristic—the time necessary for the attainment of maximum pressure. For primary alcohols, this value averages 60 minutes, for secondary alcohols, 30 minutes, and for tertiary alcohols, 20 minutes.

For primary alcohols the value $(dp/dt)_{\max} \cdot t = K$ is about 400 k.m. when alumina is catalyst; there is only one reaction taking place, dehydration to olefin and water. With alumina the reaction goes only half as fast as it does in the presence of iron, perhaps because in the latter case there are two reactions, dehydration to olefin and water and dehydrogenation to aldehyde and hydrogen. For secondary and tertiary alcohols the value K is consider-

TABLE 29

DIMETHYLETHYL CARBINOL

Expt. No.	Time, MIN.	T., °C.	p, ATMS.	p, FINAL ATMS.	CATALYST	ANALYSIS OF GAS IN %						AMT. OF GAS, L.	AMT. OF LIQUID, G.
						C_nH_{2n}	CO_2	O_2	CO	H_2	C_nH_{2n+2}		
364	100	400	100		Cu tube Al_2O_3			No gas				No gas	26 g. Amylene
365	"	"	"		"	9.3	1.8			8.0	80.0	2.0	25 g. Amylene

Table XXIII, Curve XXIII			*Table XXIV, Curve XXIV*		
TIME, MIN.	T., °C.	p, ATMS.	TIME, MIN.	T., °C.	p, ATMS.
0	300		0	360	
10	350	12	5	390	11
15	370	22	10	415	23
20	385	46	15	430	49
25	388	54	20	447	63
34	391	78	30	482	92
40	402	92	40	520	111
50	400	97	50	540	129
60	401	100	60	540	131
70	400	100	75	540	132
80	380	99	210	540	132
100	400	100			

ably less than for primary alcohols. For the latter, the equation $(dp/dt)_{\max} \cdot t = K$ is an equilateral hyperbola when $(dp/dt)_{\max}$ is plotted against t.

In conclusion, it might be added that high pressure technique is applicable to the study of the dissociation of many organic compounds and by this method it may be possible to recognize intermediate steps which would otherwise escape us. We made the first attempt to study the equilibria arising from the catalytic decomposition of alcohols under pressure.

At the present time it would be very desirable to apply the method to the determination of the energy of activation for the catalytic decomposition of various classes of organic compounds.

These experiments on the catalytic decomposition of alcohols in the presence of alumina indicate, without doubt, that the first reaction is the formation of ether by the liberation of water from two molecules of alcohol. This reaction is reversible. Subsequently, decomposition of the ether leads to the formation of olefin and water. Probably, if the alcohol were subjected to the full effect of the high temperature immediately, then the molecule of alcohol might lose water with direct formation of olefin.

It was interesting to determine whether the second reaction of decomposition—decomposition of ether into olefin and water—is also reversible and with this purpose in mind the hydration of amylene with water under the influence of alumina was investigated.[1]

In more recent years attempts have been made to realize the direct hydration of olefins into alcohols. For instance, an English patent by Smith and Bridger states that ethylene can be converted into alcohol (10% yield) by heating ethylene under pressure in contact with water containing inorganic salts—cupric chloride, mercuric chloride, or silver nitrate—the function of the salt being to increase the water solubility of the ethylene. Another English patent (Slade, 1928) claims that ethyl alcohol is formed by passing ethylene and water at 400–500° and 3000 lbs./sq. inch over certain catalysts such as thoria, phosphoric acid, or activated charcoal.

DEHYDRATION OF POLYATOMIC ALCOHOLS

The catalytic dehydration of glycols was accomplished by me in 1903.[2] The result is the same, whether the vapors of ethylene glycol are passed through a copper tube filled with alumina, or whether the glycol is heated in the high pressure apparatus at 400°. Glycol is decomposed rapidly (see table), and the value of $(dp/dt)_{\max}$ is between 4 and 5.5. One hour of heating in the autoclave is sufficient to bring about complete decomposition.

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[1] Ipatieff, Ber., *42*, 2090 (1909).

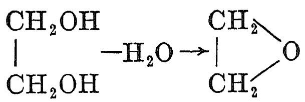
[2] Ipatieff, J. Russ. Phys. Chem. Soc., *35*, 542 (1903); *36*, 3892 (1906).

TABLE 30

Experiment 395		*Experiment 399*	
Time, Min.	Pressure, Atms.	Time, Min.	Pressure, Atms.
5	8	5	6
10	11	10	10
15	15	15	18
20	19	20	33
25	30	25	53
30	58	30	61
35	62		
75	80		
155	86		

The products of decomposition consist of water and an organic liquid which is a mixture of acetaldehyde, paraldehyde, and a small amount of crotonic aldehyde. This liquid after drying over potassium carbonate, boiled at 40–106°, the greater portion distilling at 60–90° and a smaller fraction at 90–103°. Both of these fractions reacted with sodium bisulphite and reduced ammoniacal silver hydroxide. For further identification, they were oxidized by freshly precipitated silver oxide and the silver salts were analyzed. The salt from the lower boiling fraction contained 63.27% of silver and that from the higher fraction, 61.85%; calculated for acetic acid 64%; for crotonic acid 54%. It is evident that the first fraction consisted of acetaldehyde (and paraldehyde) which was oxidized by silver oxide to silver acetate and as for the higher boiling fraction, the lower percentage of silver in the salt coupled with other tests made directly upon the material, indicated that it was crotonic aldehyde.

Passing now to the mechanism of the dehydration of ethylene glycol in the presence of alumina, we may assume that the first step consists in the formation of ethylene oxide, which, under the influence of alumina, as shown by my experiments with Leontovitch, isomerizes into acetaldehyde.



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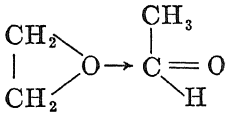


II

Acetaldehyde, as subsequently shown experimentally, is capable of polymerization to paraldehyde in the presence of alumina. The presence of crotonaldehyde can be explained in similar manner, namely, that acetaldehyde underwent aldol condensation in the presence of alumina to form acetaldol which in turn lost water to yield crotonaldehyde.

$$2CH_3CHO \rightarrow CH_3CHOHCH_2CHO \rightarrow CH_3CH{=}CHCHO + H_2O$$

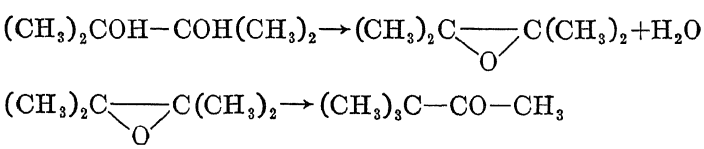
The above mechanism was proposed in 1906, and, later, during the study of the action of catalysts upon ethanol,[1] it received complete justification.

Pinacone

When pinacone is heated with alumina at 300–320° in the high pressure apparatus it loses water to form pinacolene (b.p., 102–104°).

$$(CH_3)_2COH— \qquad _2 \rightarrow H_2O + (CH_3)_2C—CO—CH_3$$

The latter was further identified by conversion into crystalline pinacolene bromide. The mechanism of the dehydration of pinacone consists of two steps, (1) dehydration to hexylene oxide, and (2) rearrangement to pinacolene.



DEHYDRATION OF CYCLIC ALCOHOLS

In order to study the effects of alumina on cyclic alcohols, some preliminary experiments [2] were first made with menthol, borneol, and cyclohexanol, and it was found that cyclic alcohols, in which a methylene group is adjacent to a hydroxyl group attached to the benzene ring, eliminate water under the catalytic influence of alumina to give good yields of unsaturated hydrocarbons.

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[1] Ipatieff and Klukvin, Ber., *58*, 4 (1925).

[2] Ipatieff and Leontovitch, J. Russ. Phys. Chem. Soc., *35*, 606 (1903).

Both mono- and dihydroxy cyclic alcohols were examined and the course of the reaction was followed by the pressure developed within the bomb.

The first experiments were with cyclohexanol,[1] $C_6H_{11}OH$, 20 g. of which was heated at 330° in a copper tube in the high pressure apparatus with 3 g. of alumina for 75 minutes. Two products were obtained, water and a hydrocarbon the boiling point of which and other properties indicated that it was tetrahydrobenzene, C_6H_{10}. It added bromine and was converted into a crystalline nitrosate by the action of amyl nitrate and nitric acid. The following experiment was carried out with a larger quantity of cyclohexanol.

One hundred grams of cyclohexanol and 10 g. of alumina were placed in the bomb and hydrogen was pumped to a pressure of 40 atmospheres, this gas being added in order to have pressure at the beginning of the experiment. It was noted that dehydration took place without the formation of tarry products and, under the conditions of the experiment, hydrogen did not act upon the double bond. The reaction was run at 300–350° and 90 g. of hydrocarbon was obtained which distilled at 82–84°, and gave the following analytical values:

$$C,\ 87.45\%;\ H_2,\ 12.20\%;\ d_{20},\ 0.8021;\ M.R.,\ 45.63$$

On treatment with amyl nitrate and nitric acid it gave a crystalline nitrosate of melting point 149°.

Borneol, on heating with alumina at 330°, gave camphene which distilled chiefly at 155–165° and did not solidify in a cooling mixture.

Menthol (Kahlbaum) was heated at 370° in the high pressure apparatus in a copper tube for 2 hours, 80 g. of menthol and 5 g. of alumina being taken for each experiment. After drying with calcium chloride, the menthene (130 g.) was distilled through a column; 50 g. distilled at 163–165°, the following 50 g. at 165°, and 25 g. at 165–167°. Eight cc. of acetic acid and 5 cc. of ethyl nitrate was added to 6 cc. of the product, and then to this mixture was added a solution of 2.4 g. of hydrogen chloride in 6 cc. of acetic acid. One gram of nitrosyl chloride was obtained, which, after crystallization from chloroform, melted at 136–137°. Doubtless, the dehydration product was a mixture of isomeric menthenes.[1]

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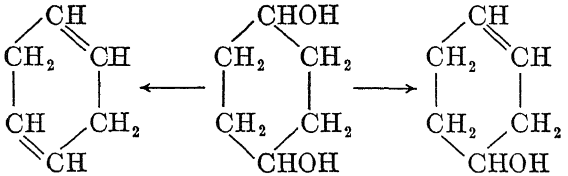
[1] Ipatieff, J. Russ. Phys. Chem. Soc., *37* (1905).

Dehydration of Cyclohexandiol

Cyclohexandiol (II) was obtained by the hydrogenation of hydroquinone in the high pressure apparatus in the presence of nickel oxide. It was heated with alumina (10% as much alumina as alcohol) in the bomb at 350° in an atmosphere of hydrogen for 3–4 hours; dehydration took place with the formation of unsaturated hydrocarbon. The liquid product, after drying with calcium chloride, was distilled into two fractions, the greater portion boiling at 80–86°, a smaller amount at 161–167°. The main reaction product was dihydrobenzene (I) d_4^{20}, 0.8311. With bromine it gave a crystalline tetrabromide, with sulphuric acid a violet coloration. Judging from the boiling point, the dihydrobenzene contained several isomers. The small fraction boiling at 161–167°, according to analysis and other criteria, was tetrahydrophenol (III) which was formed by the elimination of one molecule of water from cyclohexandiol.



I II III

Tetrahydrobenzene was obtained in very good yield from cyclohexanol which, in turn, had been prepared by the hydrogenation of phenol with nickel oxide in the high pressure apparatus. One hundred grams of cyclohexanol and 10 g. of alumina were heated in the high pressure apparatus for 6 hours at 350° under an initial pressure of 40 atms. of hydrogen; 90 g. of hydrocarbon of boiling point 82–84° was obtained. Carbon-hydrogen analysis, d_4^{20} of 0.802, M.R. of 45.63, and its crystalline nitrosate melting at 149°, all furnished evidence that the substance was tetrahydrobenzene.

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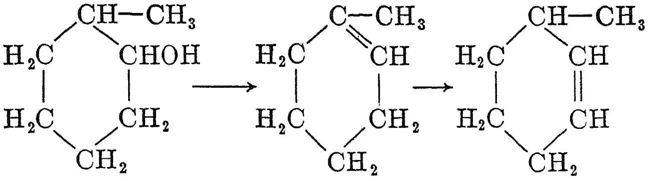
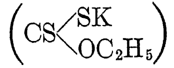
[1] Senderens' first communication on the use of alumina as dehydrating catalyst appeared in 1908 (Compt. rend., *146*, 125; *149*, 213) when he stated that slightly ignited alumina was superior to amorphous phosphorus which he had preferred before. As far as the experimental results were concerned he substantiated my previous findings. Ber., *35*, 1057 (1902); *36*, 1990 (1903).

Methylcyclohexene was obtained in excellent yield from o-methylcyclohexanol, which in turn had been prepared from o-cresol by hydrogenation in the high pressure apparatus with nickel oxide as catalyst. The cyclohexanol was dehydrated with alumina under pressure and the resultant hydrocarbon had the following characteristics—b.p., 96–110°; d_4^{20}, 0.8118; M.R., 53.76. Carbon-hydrogen analysis completed the evidence as to its formula. The boiling point indicated that the product was not a single compound, but consisted of several isomers the formation of which can be explained by the removal of water from different positions, and also by the subsequent isomerization of the unsaturated hydrocarbons under the influence of alumina as was shown to be possible by my experiments with isopropylethylene.[1]



o-Methylcyclohexanol Methylcyclohexene

The methylcyclohexene gave a crystalline nitrosate melting at 114–115°. On treating the hydrocarbon with nitrosyl chloride a crystalline product, $C_7H_{12}NOCl$ was formed, which, after crystallization from ether and benzene, melted at 104°.

In order to determine approximately the amount of methylenecyclohexene which could be present in the methylcyclohexene I treated the latter with a 1% solution of potassium permanganate according to the procedure of Favorsky and Borgman.[2] No primary-tertiary glycol was found in the oxidation product which means that no methylenecyclohexene was present. I tried to obtain the same methylcyclohexene from methylcyclohexanol by means of the xanthate  $\left(CS\begin{matrix}\diagup SK\\ \diagdown OC_2H_5\end{matrix}\right)$ method of Tchugaev [3] starting with methylcyclohexanol boiling at 164.5–165°. Two products were obtained, a small amount boiling at 98–103° and the greater amount at 103–106°, d_4^{20} being 0.8059. The nitrosyl chloride obtained from the latter melted at 107°. These data show that the xanthate method also yields an impure product.

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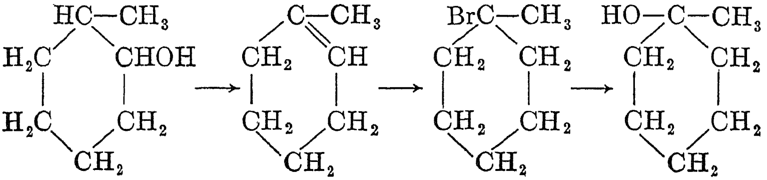
[1] Ipatieff, Ber., *36*, 200 (1903).

[2] Favorsky and Borgman, J. Russ. Phys. Chem. Soc., *39*, 1218 (1907).

[3] Russian Dissertation (1903). Investigations in the Field of Terpenes.

A different result is obtained when the methylcyclohexanol is dehydrated at lower temperature, a reaction which can be accomplished by the action of a mixed catalyst, alumina-copper oxide.[1] When o-hexahydrocresol (I) was treated with this double catalyst under an initial pressure of hydrogen, dehydration took place at 240° to give an excellent yield of unsaturated hydrocarbon (II) which consisted chiefly of one isomer—methylcyclohexene-1, 2—the properties of which agreed with those of Markovnikov's hydrocarbon. To prove its structure, the unsaturated hydrocarbon was converted into the monobromide (III) by means of hydrogen bromide and the bromide, in turn, was hydrolyzed to the alcohol (IV). It was evident by the properties that both the bromine atom and the hydroxyl group were attached to a tertiary carbon atom.



I II III IV

The nitrosyl chloride, prepared from amyl nitrate (3 volumes), methylcyclohexene (2 volumes), and two volumes of hydrochloric acid (1:19), after crystallization from benzene melted at 102°.

Anal. Calcd. for $C_7H_{14}NOCl$: N, 8.56. Found: N, 8.60. The nitrosyl chloride is rather unstable, it loses hydrogen chloride when kept in a dissicator, and changes into the oxime.

Anal. Calcd. for $C_7H_{12}NOH$: N, 11.02. Found: N, 10.92. Methylcyclohexene nitrosate obtained from a mixture of 2 g. of the hydrocarbon, 3 g. of amyl nitrate, 4 g. of acetic acid, and 2 g. of nitric acid (*d*, 1.4), after crystallization from benzene melted at 115°.

Anal. Calcd. for $C_7H_{13}N_2O_4$: N, 14.73. Found: N, 14.63. Methylcyclohexene bromide was obtained by slowly pouring the hydrocarbon into a cold acetic acid solution of hydrogen bromide, the mixture being stirred constantly. After washing with water and drying, the product distilled at 156–160°, the yield being 91%

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[1] Ipatieff and Rutala, J. Russ. Phys. Chem. Soc., *44*, 1692 (1912); C.A., *7*, 1159 (1913).

of the theoretical. When freshly distilled the product was a colorless liquid, but on standing, it quickly became brown.

Physical Constants: d_4^{18}, 1.2544; n_D^{18}, 1.48168.

Methylcyclohexanol was supposed to result from the hydrolysis of the above bromide on heating with freshly precipitated silver oxide at 100°, but 23 g. of bromide gave only 1 g. of liquid which had the characteristics of an alcohol (b.p., 153–160°). The rest of the product was methylcyclohexene-1, 2; b.p., 107–108.5°; d_4^{18}, 0.8102; n_D^{18}, 1.43943; melting point of nitrosate, 115°.

Such easy elimination of hydrobromic acid from the bromide testified to the tertiary position of the bromine atom.

The acetate of methylcyclohexanol was obtained by heating silver acetate with methylcyclohexene bromide on a water bath for 10 hours. After steam distillation followed by drying, the product boiled at 108–110°, only a small fraction distilling at 182–187°. The first fraction was methylcyclohexene (d_4^{18}, 0.8155; n_D^{18}, 1.44134); the higher boiling fraction had the properties of an ester.

Anal. Calcd. for $C_9H_{16}O_2$: C, 69.2%; H_2, 10.3%. Found: C, 69.1%; H_2, 10.2%; d_4^{18}, 0.9536; n_D^{18}, 1.4386; M.R., 43.0.

The very small yield of ester was also evidence for the tertiary character of the bromine atom. Hydrolysis of the ester with alcoholic alkali yielded a methylcyclohexanol boiling at 159–164°.

Anal. Calcd. for $C_9H_{14}O$: C, 73.3%; H_2, 12.3%. Found: C, 73.6%; H_2, 12.3%; d_4^{18}, 0.9417; n_D^{18}, 1.4517; M.R., 32.65.

This alcohol contained a tertiary hydroxyl group according to Deniges' test since it gave a yellow precipitate with this test reagent. Hexahydrocresol acted altogether differently, slowly yielding a white crystalline precipitate.

I tried to obtain evidence as to the structures of the alcohol and the bromide by preparing the bromide of hexahydrocresol by means of phosphorus tribromide. But in spite of careful heating, hydrogen bromide was liberated and the product was a mixture of bromide and methylcyclohexane. Also, there was the phenomenon of isomerization which rendered this reaction useless for the investigation of the structure of these alcohols and bromides.

Octa-hydronaphthalene was obtained from decahydronaphthol by heating under pressure for 10 hours at 350° with alumina, the decahydronaphthol having been prepared by the high pressure hydrogenation of naphthol in the presence of nickel oxide. One hundred grams of decahydronaphthol (b.p., 243–248°) was heated with 6 g. of alumina under an initial hydrogen pressure of 40 atms.; the crude product boiled at 195–215°, the main fraction at 197–199°. The latter had a density of 0.9103 at 20°, molecular refraction of 70.8, and analyzed for $C_{10}H_{16}$.

Potassium permanganate solution was decolorized at once and a nitrating mixture acted vigorously upon the hydrocarbon. A crystalline nitrosate could not be obtained with amyl nitrate and nitric acid. By means of an acetic acid solution of hydrogen bromide, a monobromide was obtained which distilled at 95–100° under reduced pressure and which decomposed on distillation at ordinary pressure. By the addition of bromine to an ether-alcohol solution of the hydrocarbon, a dibromide was obtained which melted at 169° after crystallization.

EFFECT OF PRESSURE UPON CATALYTIC REACTIONS [1]

In the decomposition of alcohol in a closed system in the presence of alumina, the effect of pressure is to slow down the catalytic decomposition, as it is clearly shown by my experiments.

The effect of pressure upon the decomposition of primary alcohols is marked—not only is the speed of decomposition diminished, but at the same time the reaction is different at certain temperatures, stopping at the ether stage:

$$2C_nH_{2n+1}OH \rightleftharpoons C_nH_{2n+1}OC_nH_{2n+1} + H_2O$$

This decomposition into ether represents a reversible dissociation [2] which takes place at constant volume. Also, in the case of alcohol decomposition in the presence of iron, the effect of pressure is to decrease the speed of decomposition. Usually, the initial pressure was small, increasing gradually, as the temperature rose and the decomposition progressed, to a final value which depended on the extent of decomposition and upon the temperature. The decomposition products can react with each other and also with the starting material, and in order to determine the effect of pressure upon the basic catalytic reaction it was necessary to start with a known pressure within the system. For this purpose various gases were employed which can be either decomposition products of the reaction in question or they can be inert gases such as nitrogen, etc.

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[1] Ipatieff, J. Russ. Phys. Chem. Soc., *38*, 75 (1906); C.A., *1*, 1538 (1907).

[2] Ipatieff, Ber., *37*, 2986 (1904).

In order to carry out such experiments it was first necessary to have a pressure pump. The pump which I used in these experiments was ordered from the Société Générale des Instruments Physiques, Genève, and it was supposed to be capable of delivering gas at a pressure of 180–200 atmospheres. The original valve had to be replaced by a steel valve of special construction and after this change, the pump worked nicely at 150 atmospheres. The gases were stored in ordinary zinc gasometers, and were dried with calcium chloride before being pumped into the reaction vessel; of course, a certain amount of gas had to be wasted in order to replace air from the pump.

A number of experiments were made on the decomposition of ethyl alcohol with iron as catalyst, the initial pressure being furnished by hydrogen, carbon dioxide, and nitrogen. These gases were pumped into the apparatus to various pressures. The data for these runs are presented in the following table. Under the heading p_0 is given the initial pressure in atmospheres of the gas introduced into the apparatus, and following is the pressure of the gas at 350°, which is slightly above the temperature at which ethyl alcohol begins to decompose. The purpose of Experiments 382, 388, 391, and 436 was to study the catalytic decomposition of alcohol by iron in the absence of foreign gas.

The following conclusions can be drawn from the data obtained on the decomposition of ethyl alcohol.

(1) It is impossible to determine the effect of pressure upon the catalytic decomposition of alcohol in the presence of iron when the reaction takes place in atmosphere of hydrogen. The experiments indicate, without doubt, that hydrogen at temperatures above 450°, in the presence of iron hydrogenates the products of decomposition—aldehyde, carbon monoxide, and olefins—converting them into saturated hydrocarbons. For example, on comparing Experiments 388 and 389, it is clear that about 2.4 liters of hydrogen were consumed in hydrogenation. In Experiment 389, 11 liters of hydrogen were charged into the bomb and according to Experiment 388 an additional 2.1 liters should be formed by the decomposition of the alcohol. Consequently the total amount of hydrogen should be 13.1 liters whereas only 10.7 liters of hydrogen were obtained. From Experiments 390 and 391, which were run at 450°, it follows that about 3 liters of hydrogen were consumed in reduction.

TABLE 31

Expt. No.	p_0, Initial Pressure, Atms.	T., °C.	p_{max}, Atms.	Time, Min.	Gas Introduced	Gas Analysis in %						Press. after Cooling, Atms.	Gas, Liters	Liquid, Grams
						CO_2	C_nH_{2n}	O_2	CO	H_2	C_nH_{2n+2}			
378	26	500	271	300	Hydrogen	8.3	11	1.5	7.3	37.4	46.0	65	15.50	20
383	25/100	500	270	350	"	4.8	1.0	1.5	9.6	41	42	61	17.20	25
380	49/122	490	255	230	"	2.2	0.8	1.4	6.6	62.0	26.6	60	15.5	23
389	50/150	468	276	310	"	0.6	3.0	1.4	5.0	64.7	25.2	68.5	16.6	36
381	80/181	500	330	165	"	0.6	1	1.4	4.8	69.0	23.2	90	22.2	27
390	75/190	450	292	310	"	0.4	0.6	1.4	2.4	80	15.6	81	19.45	35.5
382	6/59	500	223	330		9.4	1.4	1.5	11	25	49.4	48	14.0	20
388	0/90	470	129	330		4.4	15.0	1.6	7.6	42.6	28.4	20	5.0	28
391	0/60	450	142	385		2	13.6	1.2	10.4	42.2	29.2	21	5.45	34
392	45/147	445	278	320	Carbon dioxide	60.2	9.0	1.2	4.8	12.2	12.2	50	17.6	34
429	78/190	450	351	205	Nitrogen	1.2	1.4	1.6	30	5.6	17.4	93	25.2	32
433	78/204	450	350	235	"	1.4	2.0	1.8	3.4	7.8	14.8	95	25.8	33
436	0/60	450	142	275		3.0	13.2	1.8	12.6	38.0	30.8	16	4.2	33

Experiments 378, 382, and 383 show that at 500° under an initial pressure of 20 atms. of hydrogen, about 3 liters of hydrogen were used up in reduction. Gas analyses showed that the final carbon monoxide and olefin content is smaller when the reaction is run in the presence of hydrogen.

(2) The higher the pressure and the higher the temperature, the more fully are the decomposition products reduced by the hydrogen.

(3) The course of the catalytic decomposition of alcohol is not changed by the introduction of an initial pressure of 50 atms. of carbon dioxide.

(4) Introduction of nitrogen up to a pressure of 78 atms. does not influence the course of the catalytic decomposition of alcohol.

From Experiments 429, 433, and 436 it follows that 17 liters of hydrogen were taken and that about 4 liters of decomposition products should be formed, i.e., altogether there should be about 21 liters of gas finally present; actually there were 21.8 liters. The initial pressure before heating was 78 atms., and by the decomposition of alcohol (Expt. 436) 16 atms. should be obtained, or a total of 95 atms.; the actual pressures were 95 and 93 atms.

A systematic study of the decomposition of alcohols in the presence of inert gases should be made so as to ascertain if the reaction will take place under still higher pressures and also at other temperatures. First, however, a study should be made of the reactions which take place between the various products of decomposition.

In the decomposition of alcohol in iron tubes at high pressure the liquid product consisted of two layers, the lower layer being water, aldehyde, and undecomposed alcohol, and the upper layer a transparent oil, the quantity of which depended upon the operating conditions. The higher the temperature, the smaller was the upper layer and at 600° it disappeared altogether. The boiling range of the upper layer was 70–250° and above, and analysis showed the formula to be C_nH_{2n}. I assumed that this layer consisted of polymerized ethylene, and in order to test this assumption, a series of experiments was made in which ethylene was subjected to high temperature and pressure. The experimental results justified the assumption; a liquid was obtained.

The experiments of Day [1] have shown that ethylene polymerizes very slowly at ordinary pressure. When ethylene was slowly passed through a tube at 350–400° a liquid product and ethane were formed, but a decomposition, during which methane was formed, was also observed. These experiments were made at ordinary pressure and no attention was directed to any catalytic effect. An experiment was made in which ethylene was passed through a tube containing powdered aluminum. The temperature was 520–560° and 4.5 liters of ethylene was passed during 2.5 hours. A very small amount of unsaturated liquid was obtained; the gas analyzed as follows:

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[1] Day, Am. Chem. J., *8*, 153 (1886).

$$C_nH_{2n}, 86.5\%; H_2, 8.8\%; CH_4, 3.6\%$$

On passing the gas into bromine, a bromide was obtained which was practically pure ethylene bromide. This experiment indicates that ethylene decomposes very slowly, even with long contact time and high temperature, and in order to prepare significant amounts of product, the ethylene must be passed very slowly indeed.

It is a completely different picture when ethylene is heated in a closed vessel under pressure. For instance, at 400–450°, the polymerization of ethylene is quite rapid but the decomposition of ethylene into methane, hydrogen, and ethane is relatively slow.

Ethylene for these experiments was prepared by the catalytic decomposition of ethyl alcohol in the presence of alumina. Dry ethylene was pumped into the high pressure apparatus to the desired pressure, and the bomb was then heated to a given temperature; data on these experiments are presented in Table 32.

The first series of experiments has to do with the polymerization of more or less pure ethylene, whereas the second series deals with the polymerization of ethylene in the presence of hydrogen since the decomposition of alcohol took place in the presence of hydrogen. The third series of experiments constitutes a preliminary survey of the effect of reduced metals upon the polymerization of ethylene.

The heading p_o, in Tables 32 and 33 indicates the initial ethylene pressure, the same amount of ethylene being used in all the experiments—501, 502, and 503—about 40 liters. The ethylene contained a small amount of impurity (3–4%) which explains the presence of small amounts of oxygen, carbon monoxide, and carbon dioxide in the reaction products.

TABLE 32

Expt. No.	Initial Pressure, Atms.	T., °C.	Time, Min.	p_{max}, Atms.	p_{min}, Atms.	Gas Introduced, Atms.		Catalyst	Gas Analysis in %						Final p, Atms. after Cooling	Gas, Liters	Liquid, Grams
						C_2H_4	H_2		CO_2	C_nH_{2n}	O_2	CO	H_2	C_nH_{2n+2}			
404	60	400	210	208	124	Ethylene		Fe	1.4	77.4	1.6	0.2	2.4	17.0	41	17.30	20
408	50	450	105	163	65	"		Cu	0.8	49.2	1.6	0.2	3.4	43.0	20	5.00	15
501	60	460	220	300	101	"		Cu	1.4	59.2	1.0	1.4	5.4	31.4	26	8.10	25
502	60	430	340	299	103	"		Cu	1.6	79.2	0.8	1.6	3.0	14	32	11.20	21
503	60	458	180	250	79	"		Fe	1.4	57.0	1.2	1.0	4.0	34.8	25	7.80	27
393	48	450	240	92	70	23	25	Fe	1.4	4	2.0		60.2	31.6	31	8.80	Present
394	74	460	330	160	108	39	35	Fe	1.2	7.8	2.0		51.6	37.6	39	11.20	6
396	75	460	320	168	106	40	35	Fe	0.6	9.2	1.2		46.4	42.4	35	11.10	8.5
410	72	460	140	156	118	35	37	Fe	1.0	6.2	1.2		53.0	38.4	41	12.40	4
420	65	240	345	160	70	33	32	Red. Cu		14.4	1.2		26.6	57.8	38	8.20	
413	71	120	65	71	56	23	35	Red. Ni		1.4	1.0		48.2	48.2	41	12.35	

TABLE 33

Expt. No. 404			*Expt. No. 501*			*Expt. No. 502*			*Expt. No. 503*		
Time, Min.	T., °C.	p, Atms.	Time, Min.	T., °C.	p, Atms.	Time, Min.	T., °C.	p, Atms.	Time, Min.	T., °C.	p, Atms.
0		60	0		60	0		60	0		60
30	315	171	25	250	158	30	325	223	25	305	170
40	363	195	65	375	255	40	365	254	60	448	250
45	382	201	85	442	300	50	395	280	70	446	242
50	395	207	90	456	297	70	428	299	80	458	222
55	395	208	95	456	284	80	425	298	85	458	206
70	398	200	100	456	270	90	427	293	90	458	186
80	400	192	105	456	251	95	430	290	100	456	154
90	400	185	110	456	231	110	428	271	110	456	130
100	400	178	115	452	214	120	423	257	120	458	111
110	400	170	120	452	200	125	425	251	130	451	100
120	400	163	130	458	176	135	426	245	140	450	94
150	400	149	160	456	133	145	428	233	150	454	89
180	400	134	190	456	112	175	430	203	145	454	80
210	400		210	459	103	220	430	170	180	450	79
			220	455	101	280	430	127			
						340	430	103			

$P_{\max}$ indicates the maximum pressure in atmospheres at the maximum temperature; $p_{\min}$ indicates the lowest pressure observed at the same temperature. The experiment was discontinued when the pressure had practically stopped falling. The course of the polymerization is readily seen through the aid of the curves (Fig. 16) in which pressure (in atms.) is plotted against time. The data presented show that iron and copper have about the same effect upon the polymerization of ethylene (Expts. 501 and 503).

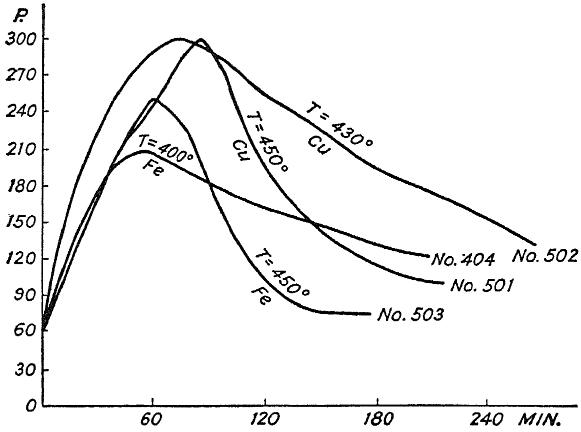

FIG. 16

Small differences in temperature have considerable effect upon the speed of polymerization as shown by the amount of liquid polymer formed and the amount of unchanged ethylene. (Cf. Table 33, Expts. 404, 501, 502, and 503.)

We see that the value $(dp/dt)_{\max}$ is changed considerably by a temperature difference of 50°, i.e., from 400 to 450°. In Experiment 404, $(dp/dt)_{\max}$ is 0.8 k.m.; Expt. 408, 4.8 k.m.; Expt. 503, 3.6 k.m.; Expt. 502, 2.6 k.m.

Simultaneous with the polymerization of ethylene there is some decomposition of ethylene into methane and hydrogen and also a certain amount of reduction to ethane, and these side reactions are more evident as the temperature increases.

As may be seen from the data presented in the table, liquid condensation product was obtained in considerable quantity; this liquid consisted of a mixture of hydrocarbons of the general formula C_nH_{2n}. The product decolorized potassium permanganate solution and also added bromine. However, liberation of hydrogen bromide was observed in the latter reaction. Distillation of 72 g. of the condensation product gave the following fractions:

1. 40–100°	9 g.
2. 100–200°	24 g.
3. 200–270°	13 g.
4. High Boiling Liquid	23 g.
Total	69 g.

The second fraction gave the following analytical results:

Anal. Calcd. for C_nH_{2n}: C, 85.7%; H_2, 14.3%. Found: C, 85.8%; H_2, 13.3%.

The question as to whether or not other hydrocarbon classes besides olefins are present was solved later. (See chapter on "Polymerization.")

In the second series of experiments ethylene was heated in an iron tube in the presence of hydrogen under pressure. Even in the presence of hydrogen, a certain amount of ethylene condensed to form liquid hydrocarbons of the general formula, C_nH_{2n}. However, very little olefinic material was found in the gas—instead, there was a considerable amount of saturated hydrocarbons, chiefly methane.

According to the data given in Table 34, it is evident that the reaction comes to a state of equilibrium, since further heating causes no change in pressure or in the percentage composition of the system. Data concerning the change in pressure with time, at constant temperature, are presented in Table 32 (Expts. 394 and 396).

The preliminary experiments on the reduction of olefins by hydrogen in the presence of reduced metals lead to the same general conclusions as the second series of experiments.

Sabatier and Senderens showed that an equimolar mixture of ethylene and hydrogen in the presence of reduced nickel produced exclusively ethane below 200°. On the other hand, I showed that in a closed vessel at 150°, there is also a large amount of methane produced; further experiments must decide whether ethylene or ethane decompose under high pressure in the presence of reduced nickel.

These experiments confirmed my belief that carbon monoxide and olefins resulting from the decomposition of alcohols in the presence of iron are reduced to saturated hydrocarbons by hydro-

TABLE 34

Expt. No. 394			*Expt. No. 396*		
TIME, MIN.	T., °C.	*p*, ATMS.	TIME, MIN.	T., °C.	*p*, ATMS.
0		92	0		100
30	350	150	30	383	157.5
60	447	159.5	40	411	168
65	457	155	45	435	168
70	460	150	50	449	163
75	460	145	55	457	160
85	460	135	60	465	151
100	460	127	65	465	141
120	460	120	70	464	133
150	460	115	90	461	122
180	458	112	120	455	113
210	458	111	180	460	110
240	460	110	270	464	107
270	458	109	295	460	106
300	458	109	320	460	106
330	456	108			

gen, whereas the liquid accompanying the decomposition products of ethyl alcohol, ethyl ether, and acetaldehyde, is formed through the polymerization of ethylene and consists of hydrocarbons of general formula C_nH_{2n}. Thus, the presence of all actual products of the high temperature, high pressure, catalytic decomposition of alcohol are understandable in the light of these reactions.

CATALYTIC DECOMPOSITION OF ALCOHOL TO BUTADIENE UNDER THE CATALYTIC INFLUENCE OF POWDERED ALUMINUM[1]

When ethanol is passed through a copper tube containing alumina which has been strongly ignited, the decomposition temperature of alcohol is found to be higher than with alumina which has not been heated so hot and the life of the ignited catalyst is short. The ethylene also is not pure, being contaminated with carbon monoxide, methane, and hydrogen. The exit gas, on bubbling through bromine at 0°, formed ethylene bromide, and also a certain amount of a higher boiling product, which, according to analysis and physical properties, must be butadiene tetrabromide.

$$=CH—CH=CH_2 + 2Br_2 \rightarrow CH_2Br—CHBr—CHBr—CH_2Br$$

At this time (1903) butadiene had already been obtained by passing isoamyl alcohol through a tube at high temperature. The gaseous products had been passed into bromine and, on distilling the bromides there was obtained the solid tetrabromide of butadiene.

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[1] Ipatieff, J. prakt. Chem., *67*, 420 (1903).

It was not theorized as to the mechanism of butadiene formation by the pyrolysis of isoamyl alcohol because the decomposition temperature was high (600°) that many reactions were possible. However, I carefully investigated butadiene formation from ethanol and was thus led to the discovery of a new pyrolytic reaction of ethanol, promoted by powdered aluminum.

When ethanol is passed over powdered aluminum at 600°, a special sort of decomposition takes place; besides acetaldehyde and ethylene there is a considerable amount of a diolefin, butadiene, $CH_2{=}CH{-}CH{=}CH_2$. The exit gas was passed into bromine, and when the ethylene bromide was removed by distillation, the solid tetrabromide of butadiene remained, $CH_2BrCHBrCHBrCH_2Br$, melting point 115–116°. The parent diolefin was obtained by treating the tetrabromide with zinc dust and alcohol. This diolefin reacted with a saturated solution of hydrogen bromide in acetic acid to yield an unsaturated bromide, boiling point 102–107°. This bromide added bromine and decolorized potassium permanganate solution. It analyzed for $CH_3CHBrCH{=}CH_2$ which confirms the structure of the original diolefin as butadiene-1, 3.

The following experiment illustrates the decomposition of ethanol as brought about by aluminum. One hundred and thirty-six grams of absolute alcohol was passed in 50 minutes through a glass tube charged with powdered aluminum and maintained at 580–600°. Nine grams of acetaldehyde and a certain amount of water condensed, the gas being bubbled through bromine. Eighty-five grams of bromide was obtained, and after distilling off the ethylene bromide, 8 g. of butadiene tetrabromide (m.p., 115–116°) remained.

Gas Analysis. Unsaturated, 44.8%; CO_2, 0.9%; CO, 3.5%; CH_4, 6.3%; H_2, 43.5%.

Contact time and temperature play an important part as regards the yield of butadiene. At my suggestion, this study was continued by Gdanovitch [1] and the following explanation was finally accepted. The first reaction is the formation of ether, catalyzed by the trace of aluminum oxide always present on the surface of the aluminum.

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[1] Gdanovitch, J. Russ. Phys. Chem. Soc., *36*, 765 (1901).

$$2C_2H_5OH \rightarrow C_2H_5OC_2H_5 + H_2O$$

The second reaction is the catalytic decomposition of ether into butadiene, catalyzed by the aluminum.

$$C_2H_5OC_2H_5 \rightarrow H_2O + CH_2{=}CHCH{=}CH_2$$

My co-worker Filippov tested this proposed mechanism by passing ether over powdered aluminum and he obtained better yields of butadiene than when starting with ethanol.

Thus, we have a third kind of catalytic decomposition of ethanol.

$$2C_2H_5OH \rightarrow CH_2{=}CHCH{=}CH_2 + 2H_2O$$

In contrast with the other two decompositions, it has not yet been obtained as the sole reaction, but this goal may be realized by further study and especially through the aid of promoters. The reaction was studied later by Lebedev who improved the yield, using a mixed catalyst, to such an extent that this reaction was applied to the commercial production of butadiene for the manufacture of synthetic rubber.

CHAPTER III

CATALYTIC DECOMPOSITION OF ACIDS[1]

I studied the dehydration of organic acids by alumina in 1903–1904. Later, in 1908 and 1913, Senderens[2] also investigated this field and completely confirmed my findings.

Acetic acid starts to decompose in a copper tube at 700°; this is purely a pyrogenetic .decomposition. But the decomposition of acetic acid is altogether different in the presence of various catalysts. I studied the following catalysts: zinc, iron, alumina, sodium hydroxide, zinc oxide, and the carbonates of zinc, barium, calcium, and strontium. Of these catalysts, barium carbonate had been proposed by Squibb for the decomposition of acetic acid into acetone. The others were first studied by me, and much subsequent work was done by other investigators. I mention these pioneering investigations to show that I realized, and called attention to the fact, at the very start of my studies, that there existed a certain relationship between the chemical properties of catalysts and their actions upon organic compounds. Thirty years ago it was difficult to find this relationship, but all our experiments showed us that such a relationship existed and my efforts were directed, from the beginning, to the solution of this question.

A number of experiments on the decomposition of acetic acid at ordinary pressure in the presence of various catalysts are summarized in Table 35. The amount of the acid in each experiment was 90–100 g.

Acetic acid, in the presence of various catalysts, undergoes two types of decomposition, *ketonic* decomposition and *decarboxylization.*

The ketone, however, is not the decomposition product of the acid molecule itself; it is formed either from two molecules of acid or from the salt.

$$2CH_3COOH \rightarrow H_2O + CO_2 + CH_3COCH_3$$

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[1] **Ipatieff, J. Russ. Phys. Chem. Soc., *35*, 543 (1903).**

[2] **Senderens, Bull. soc. chim., (4), *3*, 824 (1908).**

TABLE 35

CATALYST	T., °C.	TIME, MIN.	ACETONE, G.	GAS, L.	GAS ANALYSIS IN %				
					CO_2	CO	H_2	CH_4	C_nH_{2n}
Zn	560	60	35	13.5	87.2		10.8	2.0	
Zn	570								
ZnO	570	70	30						
$ZnCO_3$	560	60	21		88.0			7.2	
$CaCO_3$	580	60	30		92.7				
$StCO_3$	580	60	32		80.8				
$BaCO_3$	530	60	15		72.4				
$CaCO_3$	530	50	26		87.0				
NaOH	540	45	8		19.0		15.3	60.7	4.4
Na_2CO_3	540	30	15		63.0		6.9	27.0	2.8
Fe	550	50	Traces		19.6	30.1	36.3	10.9	2.8

But, for the sake of brevity, we will retain the term *ketonic splitting of acid.* Of all the different types of decomposition, the ketonic gives the best yields, up to 75% of the theoretical, the chief products being ketone, water, and carbon dioxide. The ketone, at the moment of formation, may decompose into carbon monoxide, and saturated and unsaturated hydrocarbons. The carbonates of the metals of the second group in the periodic system are catalysts for the ketonic decomposition of acids—barium, strontium, calcium, and zinc. Zinc metal, and also its oxide, are also excellent catalysts for the preparation of acetone from acetic acid. It was already known that ketones could be obtained by the dry distillation of the calcium salts of acids, the products being calcium carbonate and ketone and this reaction has considerable practical application but it cannot be said that the yields of acetone from acetic acid are very good by this method. The reason for the poor yields doubtless lies in the fact that the acetone is not immediately removed from the reaction vessel, and consequently side reactions take place. When the vapors of acetic acid are passed at 570–580° over the carbonates of the metals mentioned above, acetone is obtained in good yield. The carbonates of barium, strontium, and calcium are unchanged, but zinc carbonate is converted into the oxide, and when metallic zinc is employed as catalyst, the metal becomes coated with a very thin layer of oxide.

Catalysis by means of carbonates is easily understood as follows. The first step consists in the formation of a salt (e.g., barium acetate) and carbon dioxide; the second step in the decomposition of the salt into carbonate and ketone; the third step is a repetition of the first step, etc. The action of zinc oxide or carbonate can be explained in the same way, the only difference being that we always find zinc oxide at the end of the reaction since zinc carbonate decomposes at 540–580° into oxide and carbon dioxide. But, in the case of metallic zinc it must be assumed that the catalyst is zinc oxide and not the free metal, else the amount of hydrogen formed would be greater than actually found.

However, it is necessary to ask one question. Why is it that the carbonates of barium, strontium, calcium, and zinc are catalysts, and also zinc oxide, but not iron, although iron is capable of forming iron acetate and the latter splits into iron carbonate and acetone?

In order to answer this question it is necessary to understand the chemical properties of iron acetate, iron carbonate, etc. Although all the necessary data are not available in the literature, such as the stability of the carbonates, the conditions of formation of the acid carbonates, etc., enough is known to enable us to fashion certain hypotheses which will direct the investigation of the mechanism of ketone formation in the presence of metallic carbonates.

In order to form a ketone it is necessary that a molecule of carbon dioxide separate from two molecules of acid and the function of the catalyst is to, at least momentarily, combine with this carbon dioxide.

Whether we assume that the acetic anhydride is formed from two molecules of acetic acid without the intermediate salt formation, or whether we assume that a salt is first formed, which decomposes into ketone and carbon dioxide, in either case it is necessary for the catalyst to have the ability to combine with carbon dioxide. Thus, the carbonates of barium, strontium, and calcium are able to combine with carbon dioxide with formation of bicarbonates. Zinc oxide is also able to add carbon dioxide to form carbonate, and metallic zinc, in the presence of air moisture and carbon dioxide, forms the carbonate.

Iron is different, as is well known; in the presence of air, moisture, and carbon dioxide, it does not form the carbonate. Iron is not a catalyst for the ketone splitting of acids but it does promote another type of decomposition.

These few data are not sufficient to enable us to entirely explain the various decompositions of acids or to predict the behavior of this or that catalyst on the basis of its chemical properties. Another question might be asked—why should a single molecule of carbon dioxide come from two molecules of acid? But if the hypothesis of intermediate salt formation corresponds to reality, then this behavior is completely understandable. If we assume that the carbon dioxide comes directly from the acid and not from the intermediate salt, then the manner of the separation of carbon dioxide depends on the character of the alkali. The more energetic the catalyst, the greater the chance that the carbon dioxide will come from a single molecule of acid, the result being a special type of acid decomposition—decarboxylization. This latter type of decomposition takes place with acetic acid when sodium hydroxide is the catalyst. But when the catalyst is sodium carbonate there is considerable formation of acetone. This is similar to the case of ethanol and sulphuric acid in which either ethylene or ethyl ether can be obtained, ethylene at high temperature and ether at low temperature. The same might be said about alumina, except that it is somewhat more complicated inasmuch as not only temperature but also pressure must be manipulated in order to separate the two reaction phases.

When gaseous acetic acid is passed through an iron tube at 550° there is, to be sure, a very small amount of acetone formed, but the main products are hydrogen and carbon monoxide. This is a special sort of decomposition and the inability of iron to catalyze the formation of acetone has been explained on the basis that iron oxide is unable to form iron carbonate under the conditions of the experiment.

The catalytic decomposition of propionic acid [1] with zinc at 590° or calcium carbonate at 530° yields chiefly diethyl ketone. The decomposition of propionic acid proceeds as readily as that of acetic acid, the chief difference being that propionic acid produces more carbon monoxide and hydrogen which may be due to the lower stability of diethyl ketone. Calcium carbonate gives the best yields of ketone from both propionic and acetic acid.

Senderens [2] studied the decomposition of organic acids in the presence of various catalysts—alumina, thoria, chromium oxide, and others. The yield of ketone drops with rise in molecular weight of the acid. Acetic anhydride gives the same results as acetic acid but the catalyst, alumina, has only a short life due to excessive carbonization.

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[1] Ipatieff, Schuman, J. Russ. Phys. Chem. Soc., *36*, 764 (1904).

[2] Senderens, Bull. soc. chim., (4), *3*, 827 (1908).

Alumina promotes the formation of mixed aliphatic-aromatic ketones when the charging material is a mixture of benzoic acid and an aliphatic acid, and here, also, increase in the molecular weight of the aliphatic acid cuts down the yield of the mixed ketone. Alumina produces a dehydrating effect not only on monobasic acids but also on dibasic acids. Thus, when oxalic acid is heated below 100° in a flask with alumina, the product is a mixture of carbon monoxide, carbon dioxide, and water. This method of preparing carbon monoxide offers certain advantages over the usual method of heating oxalic acid with sulphuric acid since the evolved gas is uniform and there is no sublimation of oxalic acid. Alumina was tested as a dehydrating agent, not only of acids but also of esters [1] and it was found that esters suffer decomposition around 300° with the formation of ketones. The ester decomposes as if it were a mixture of acid and alcohol, e.g., the decomposition of ethyl acetate is represented by the following equation:

$$2CH_3COOC_2H_5 \rightarrow CH_3COCH_3 + 2C_2H_4 + CO_2 + H_2O$$

In the absence of alumina, ethyl acetate does not decompose. The ethyl esters of propionic and higher acids decompose at 380–400° in the presence of alumina, with the formation of the corresponding ketones in better yields than from the acids themselves.

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[1] Sabatier and Mailhe, Bull. soc. chim., (4), *11*, 369 (1912).

CHAPTER IV

CATALYTIC ISOMERIZATION

The catalytic decomposition of isobutyl alcohol in the presence of alumina gives only one normal decomposition product, isobutylene, whereas the decomposition of fermentation amyl alcohol[1] in the presence of alumina yields in addition to the two normal products, isopropylethylene and methylethylethylene, also considerable trimethylethylene.

It is interesting to inquire into the reason for the appearance of trimethylethylene. One can suppose that we have here the process of isomerization. In studying the reason for the formation of trimethylethylene in the alumina catalyzed decomposition of fermentation amyl alcohol, attention must be paid to the presence of this olefin in commercial amylene made by other methods, e.g., through the action of sulphuric acid and of zinc chloride. As shown by several investigators, Flavitsky, Vishnegradsky, Eltekov, Kondakov, *et al.*, commercial amylene always contains, besides the normal decomposition products, a certain amount of other hydrocarbons which are formed either by isomerization or by different decomposition reactions. In connection with this there should be considered the non-homogeneity of the butylene obtained from isobutyl alcohol by the action of molten zinc chloride according to the method of LeBel and Greene[2] and by the action of sulphuric acid according to the procedure of Puchot.[3] Up to the time of my investigations (1903) none of the attempted explanations had been successful.

My investigations on the addition of the hydrohalogen acids to acetylene and allene hydrocarbons,[4] the study of the rules of addition of these acids to olefins in acetic acid and aqueous solutions,[5] and my study of the high temperature reactions of hydro-

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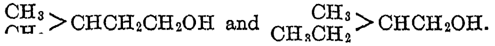
[1] Amyl alcohol of fermentation consists of



$$\genfrac{}{}{0pt}{}{CH_3}{CH}{>}CHCH_2CH_2OH \text{ and } \genfrac{}{}{0pt}{}{CH_3}{CH_3CH_2}{>}CHCH_2OH.$$

[2] LeBel, Greene, Bull. soc. chim., *29*, 306.

[3] Puchot, Ber., *13*, 2395 (1898).

[4] Ipatieff, J. prakt. Chem., *53*, 145 (1896).

[5] Ipatieff, J. Russ. Phys. Chem. Soc., *36*, 659 (1904).

carbons and alcohols as promoted by various catalysts, furnished valuable indications as to the reason for the formation of these abnormal products. These investigations offered explanations, not only for the abnormal products of the reaction of sulphuric acid and of zinc chloride with alcohols but also for the anomalies observed in the decomposition of the primary butyl chlorides.

Since isomeric transformation of unsaturated hydrocarbons may also be promoted by the action of hydrohalogen acids and since the manner of addition may depend upon the conditions, I think I may be able to discuss this subject of isomerization more clearly if I begin by describing my first experiments on the addition of hydrohalogen acids to unsaturated hydrocarbons.

ACTION OF HYDROGEN BROMIDE UPON UNSATURATED HYDROCARBONS OF FORMULA, C_nH_{2n-2}

The study of the addition of hydrogen bromide to acetylene and allene hydrocarbons was undertaken so as to be able to differentiate, as well as to separate, disubstituted acetylene from allene hydrocarbons. The experimental data that were at our disposal at this time gave no positive indications; previous experiments on the addition of hydrogen bromide to the acetylene hydrocarbons had been carried out in aqueous solution and the results did not give a true picture of the addition reactions of acetylene. I used other experimental conditions for the addition of hydrogen bromide to disubstituted acetylenes and allenes. My reagent was glacial acetic acid, saturated at 0° with hydrogen bromide, such a solution containing 48% of hydrogen bromide and fuming strongly in the air.

Methylisopropylacetylene.—An especially purified sample of methylisopropylacetylene was used in this study. The material boiled at 71–72° and gave no precipitate with an ammoniacal solution of copper chloride and alcoholic silver nitrate, i.e., it did not contain any monosubstituted acetylene. To 14 g. of this hydrocarbon was added, drop by drop at 0°, 150 g. of a 48% solution of hydrobromic acid in acetic acid. The product which separated was washed with water, dried, and distilled under a pressure of 13–14 mm. The yield was 25 g., which indicated at once that only one molecule of hydrogen bromide had added. The major portion distilled at 40° at 13–14 mm. and redistillation at atmospheric pressure gave a product boiling at 128–131°, d_0, 1.227. According to the bromine analysis the formula was $C_6H_{11}Br$. The bromide decolorized permanganate solution and did not dissolve when heated with water or aqueous potassium carbonate solution. It was an unsaturated monobromide formed according to the following equation.

$$(CH_3)_2CHC{\equiv}CCH_3 + HBr \quad \begin{array}{c} (CH_3)_2CHCBr{=}CHCH_3 \\ \text{or} \\ (CH_3)_2CHCH{=}CHBrCH_3 \end{array}$$

Thus, the disubstituted acetylene gave as chief product an unsaturated monobromide. There was a small amount of dibromide but insufficient quantity of it was isolated for the study of its properties.

Allene hydrocarbons.—A wholly different picture is obtained when hydrogen bromide adds to the allene hydrocarbons.

To 25 g. of *dimethylallene,* 163 g. of a 47% solution of hydrogen bromide in acetic acid was added dropwise at 0°, 70 g. of the crude bromide being obtained instead of 81 g. which is the theoretical yield for the addition of two molecules of hydrogen bromide. The dibromide was dried, and distilled at a pressure of 15 mm.; of 68 g. of crude product, 5 g. distilled at 40–74°, 63 g. at 74–75°.

The first fraction was treated with water until it no longer diminished in volume. The bromide which was insoluble in water resulted from the addition of two molecules of hydrogen bromide to dimethylallene. From the acid solution an unsaturated alcohol was separated by means of potash, dimethylethenyl carbinol, which was formed by the hydrolysis of the monobromide resulting from the addition of one molecule of hydrogen bromide to dimethylallene.

$$(CH_3)_2C{=}C{=}CH_2 + HBr \rightarrow (CH_3)_2CBrCH{=}CH_2$$

$$(CH_3)_2CBrCH{=}CH_2 + H_2O \rightarrow (CH_3)_2COHCH{=}CH_2$$

The second fraction (b.p., 74–75°), which was the chief product, originated through the addition of two molecules of hydrogen bromide to dimethylallene. Its density at 0° was 1.675 and its analysis confirmed the formula, $C_6H_{12}Br_2$. By the action of aqueous potash it dissolved completely, the hydrolytic product being 2-methylbutandiol-2, 4. Therefore, we must assume that the addition of two molecules of hydrogen bromide to the dimethylallene occurred as follows.

$$(CH_3)_2C{=}C{=}CH_2 + 2HBr \rightarrow (CH_3)_2CBrCH_2CH_2Br$$

Thus, we see that the addition of hydrogen bromide to dimethylallene does not take place in the usual manner. According to all probabilities the first molecule of hydrogen bromide adds to form an unsaturated tertiary bromide.

$$(CH_3)_2C{=}C{=}CH_2 + HBr \rightarrow (CH_3)_2CBrCH{=}CH_2$$

The addition of a second molecule of hydrogen bromide to this unsaturated bromide proceeds contrary to the usual rule. The usual effect of an accumulation of methyl groups does not hold, since the bromine adds to the more hydrogenated carbon atom.

It is interesting to note here that this dibromide enabled me to carry out an important synthesis of the hydrocarbon isoprene,[1] the structure of which had long been a difficult problem. This synthesis of isoprene showed that the rules which had been accepted up to this time (1896) concerning the addition of hydrogen halide acids to, and the elimination of these acids from disubstituted hydrocarbons cannot be used in the determination of structure.

The synthesis of isoprene was suggested by the observation that the dibromide obtained by the addition of two molecules of hydrogen bromide in acetic acid solution to isoprene (obtained either by the dry distillation of para-caoutchouc or by the decomposition of dipentene) was identical with the dibromide obtained under the same conditions from dimethylallene. The next step was to compare the action of alcoholic alkali upon this dibromide which could be obtained in different ways.

Thirty-nine grams of dibromide (b.p., 83–84°/20 mm.) was added to an alcoholic potassium hydroxide solution (55 g. KOH in 70 g. of 90% alcohol). After the force of the reaction had subsided, the mixture was steam distilled and the product washed with water, dried, and distilled. The first fraction (12 g.) distilled at 32–33° and a small second fraction came over at 120–121° which was an unsaturated ether, $C_5H_9OC_2H_5$.

If the elimination of hydrogen bromide had followed the then accepted rule, the dibromide formed by the addition of two molecules of hydrogen bromide to dimethylallene would have regenerated dimethylallene, boiling point 40°, on treatment with alcoholic potassium hydroxide.

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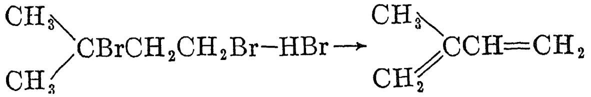
[1] Ipatieff, J. prakt. Chem., *55*, 4 (1897).

$$(CH_3)_2CBrCH_2CH_3Br—HBr \rightarrow (CH_3)_2C{=}C{=}CH_2$$

But the hydrocarbon obtained (b.p., 32–33°) was found to have different properties from those of dimethylallene and, therefore, it was concluded that the elimination of hydrogen bromide had taken place in another manner with the formation of a diolefin, e.g.,



and that isoprene must have the structure of methyl divinyl. In order to prove the identity of the hydrocarbon obtained from the dibromide of dimethylallene with isoprene from para-caoutchouc or dipentene, this hydrocarbon was treated in the cold with hypochlorous acid so as to obtain the dichlorohydrin. It was known [1] that diolefins add hypochlorous acid to give characteristic dichlorohydrins, and Favorsky and Mokievsky [2] obtained a dichlorohydrin (m.p., 81°) by the addition of two molecules of hypochlorous acid to isoprene which they had prepared by the decomposition of turpentine. My experiments on the addition of hypochlorous acid to synthetic isoprene gave almost quantitative yields of a dichlorohydrin, $C_5H_{10}O_2Cl_2$, which melted at 81°.

Similar abnormal addition of hydrogen halide acids to the allene and diethylene hydrocarbons was observed by me also in other instances. Thus, trimethylallene, on being treated with hydrogen bromide in acetic acid solution, gives a dibromide of the following structure:

$$(CH_3)_2C{=}C{=}CH(CH_3) + 2HBr \rightarrow (CH_3)_2CBrCH_2CHBr(CH_3)$$

Unsym-methylethylallene adds two molecules of hydrogen bromide, according to the following reaction:

$$CH_3CH_2(CH_3)C{=}C{=}CH_2 + 2HBr \rightarrow CH_3CH_2(CH_3)_2CBrCH_2CH_2Br$$

By the action of alcoholic alkali upon this dibromide the hydrocarbon ethyldivinyl was obtained

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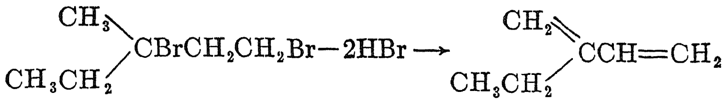
[1] Henry, Ber., *7*, 415 (1902); Przylyter, *ibid.*, *13*, 51, 2281 (1898); *ibid.*, *20*, 3241 (1905).

[2] Favorsky and Mokievsky, Chem. Zeit., No. 101 (1895).



$$\begin{array}{l}CH_3\diagdown \\ \qquad CBrCH_2CH_2Br-2HBr \\ CH_3CH_2\diagup\end{array} \longrightarrow \begin{array}{l}CH_2\diagdown \\ \qquad CCH{=}CH_2 \\ CH_3CH_2\diagup\end{array}$$

This diolefin reacted with hypochlorous acid similarly to isoprene.

Addition of Hydrogen Halide Acids to Olefins

The abnormal addition of hydrogen bromide to the allenes and to diolefins in acetic acid solution induced me to investigate this reaction also with *olefins*. It was known that the addition of hydrogen halide acids in aqueous solution or in gaseous state follows the rule formulated by Markovnikov, namely, that the halogen adds to the less hydrogenated carbon atom. The first experiment carried out with Ogonovsky,[1] on the addition of hydrogen bromide in acetic acid solution to isobutylene showed that we have here an abnormal addition of hydrogen bromide, and that acetic acid is not an indifferent solvent.

The isobutylene used in this investigation was prepared by two different methods. One method was that of Butlerov, the action of alcoholic alkali upon isobutyl iodide.

$$(CH_3)_2CHCH_2I—HI \rightarrow (CH_3)_2C{=}CH_2$$

The other method was that discovered by me, the catalytic dehydration of isobutyl alcohol by means of alumina.

$$(CH_3)_2CHCH_2OH—H_2O \rightarrow (CH_3)_2C{=}CH_2$$

The isobutylene obtained by the first method was passed through a 40% solution of hydrogen bromide in acetic acid at 0°. The bromide, after drying, distilled at 72–83°. In order to determine its constitution, it was heated with boiling water under a reflux condenser. Out of 210 g. of bromide mixture, 13 g. remained undissolved after repeated treatments, which quantity corresponds to a yield of about 6% based on the total bromide. Its boiling point was 87–95°. When isobutylene was passed through aqueous hydrogen bromide, a bromide was obtained which boiled at 72–74° and which dissolved completely in hot water in 30–40 minutes. This doubtless shows that the isobutylene under investigation was pure. It would seem that the addition of hydrogen bromide in acetic acid goes in two directions to give both a tertiary and a primary bromide.

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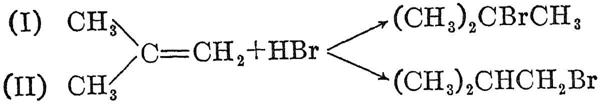
[1] Ipatieff, Ogonovsky, Ber., *36*, 1988 (1903).



$$\begin{matrix}\text{(I)}\ CH_3\diagdown\\ \text{(II)}\ CH_3\diagup\end{matrix}C{=}CH_2+HBr<\begin{matrix}\nearrow (CH_3)_2CBrCH_3\\ \searrow (CH_3)_2CHCH_2Br\end{matrix}$$

The primary bromide (II) is the abnormal product inasmuch as the halogen added to the more hydrogenated carbon. When the crude reaction product was refluxed with alcoholic alkali, the tertiary bromide was readily converted into isobutylene which was identified by its reaction with nitrosyl chloride to give the characteristic nitroso-chloride addition compound melting at 96–98°. The primary bromide (II) reacted with potassium ethylate to form ethyl isobutyl ether.

(I) $(CH_3)_2CBrCH_3 \rightarrow (CH_3)_2C{=}CH_2$

(II) $(CH_3)_2CHCH_2Br + C_2H_5OK \rightarrow (CH_3)_2CHCH_2OC_2H_5 + KBr$

This ether, a saturated compound, did not decolorize potassium permanganate solution.

Isobutylene obtained according to my catalytic method reacted quantitatively with aqueous hydrogen bromide to give tertiary bromide (I) boiling at 72–74° and completely soluble in water, which confirms the homogeneity of the original olefin. But when this isobutylene was passed into acetic acid-hydrogen bromide, there were two products, tertiary bromide and primary bromide (b.p., 91–95°). The latter reacted with alcoholic potassium hydroxide with formation of isobutyl ethyl ether. Thus, in acetic acid-hydrogen bromide, there are two simultaneous addition reactions. The chief reaction is that predicted by Markovnikov's rule, but a second reaction proceeds in such manner that the halogen adds to the more hydrogenated carbon atom.

The reason for the abnormal addition lies in the solvent, acetic acid, and it seemed interesting to me to study the behavior of other ethylene hydrocarbons. I also investigated the addition of hydrogen chloride and of hydrogen iodide in the presence of acetic acid.

Addition of Hydrogen Bromide in Acetic Acid Solution [1]

The *ethylene* which served for the experiment was prepared by the contact method, alcohol vapor being passed through a copper tube filled with alumina. Although numerous conditions were tried, ethylene could not be made to add hydrogen bromide in acetic acid solution.

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[1] Ipatieff and Dekhanov, J. Russ. Phys. Chem. Soc., *36*, 659 (1904); British C.A., 86, I, 705, 1904.

Propylene was also tried, the olefin being prepared by the catalytic dehydration of propyl alcohol in the presence of alumina. This olefin formed a very small amount of bromide but not enough to enable us to determine its nature.

The non-reaction of ethylene and propylene with HBr in acetic acid solution offers the possibility of separating these olefins from the butylenes which are readily absorbed by this reagent. Our recent investigations showed us, however, that in the presence of butylenes, propylene combines with hydrogen bromide in acetic acid and other solvents.[1]

Catalysis in the Addition of Hydrogen Bromide to Olefins

Amylenes.—The following amylenes were studied as regards reaction with hydrogen bromide; isopropylethylene, trimethylethylene, and methylethylethylene and all three were found capable of forming addition products with hydrogen bromide.

Isopropylethylene (b.p., 21–22°) was obtained by the method of Vishnegradsky and also by the contact[2] decomposition of isoamyl alcohol in the presence of alumina followed by a sulphuric acid treatment as specified by Vishnegradsky.

Isopropylethylene was slowly added with shaking to an excess of a cooled 40% solution of hydrogen bromide in acetic acid. The reaction product was separated by the addition of water and dried with calcium chloride, the yield being 90% of the theoretical amount.

Distillation of 102 g. of the crude product yielded 92 g. boiling at 113–117° and about 2 g. boiling at 117–119°.

Anal. Calcd. for $C_5H_{11}Br$; Br, 52.9%. Found: Br, 52.4%; $d_0^0 = 1.2322$.

The bromide product (b.p., 113–117°) did not dissolve when boiled under a reflux condenser with water, thus eliminating the presence of tertiary bromide. Ninety grams of bromide, treated with alcoholic alkali, yielded 15 g. of hydrocarbon and 13 g. of ether. The latter still had a trace of halogen which was removed by distillation over metallic sodium, the greater part of the ether distilling at 110–111°.

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[1] Ipatieff, Pines, Wackher, J. Am. Chem. Soc., *51*, 2398 (1934).

[2] Ipatieff, J. Russ. Phys. Chem. Soc., *35*, 577 (1903).

Analytical values and physical constants indicated that the ether was primary ethyl isoamyl ether which must have been formed from a primary bromide. That the product was not a secondary ether was also shown by the experiments of Kondakov,[1] who obtained not a secondary ether but a tertiary one with boiling point 102° by the action of alcoholic alkali on both the iodide and the bromide of methylisopropyl carbinol. However, our ether boiled at 110–111°.

In order to convince ourselves as to the identity of this ether, it was treated with hydrogen iodide at 100° in a glass stoppered flask. The product was separated into two fractions, one boiling at 80–90°, the other at 140–150°. The first fraction was ethyl iodide; the second contained primary iodide according to Mayer's test.

Treatment of these two fractions separately with alcoholic alkali yielded ether from the first and a hydrocarbon from the second. The latter did not form a crystalline compound with nitrosyl chloride and was similar in other properties to isopropylethylene. This established the fact that the original bromide was primary, having been formed by the addition of hydrogen bromide to the olefin, the halogen adding to the more hydrogenated carbon atom.

$$(CH_3)_2CHCH{=}CH_2 + HBr \rightarrow (CH_3)_2CHCH_2CH_2Br$$

$$(CH_3)_2CHCH_2CH_2Br + KOC_2H_5 \rightarrow (CH_3)_2CHCH_2CH_2OC_2H_5$$

$$(CH_3)_2CHCH_2CH_2OC_2H_5 + 2HI \rightarrow (CH_3)_2CHCH_2CH_2I + C_2H_5I$$

$$(CH_3)_2CHCH_2CH_2I{-}HI \rightarrow (CH_3)_2CHCH{=}CH_2$$

But the action of alcoholic alkali gave besides an ether also an unsaturated hydrocarbon which was identified as trimethylethylene by its boiling point and the formation of a nitrosylchloride addition compound melting at 72–73°. Thus it was evident that hydrogen bromide adds also in a second direction, according to Markovnikov's rule, to the extent of 50–60%.

$$(CH_3)_2CHCH{=}CH_2 + HBr \rightarrow (CH_3)_2CHCHBrCH_3$$

$$(CH_3)_2CHCHBrCH_3{-}HBr \rightarrow (CH_3)_2C{=}CHCH_3$$

In order to compare the addition of hydrogen bromide in both acetic acid and water solution an experiment was made using the latter solvent. The reaction proceeded very slowly in aqueous solution (isopropylethylene plus hydrogen bromide) as already noted by Vishnegradsky, and the olefin had to be contacted with several portions of acid. The small amount of bromide which was isolated did not dissolve in water. Treatment with alcoholic alkali gave almost exclusively trimethylethylene which was identified through its characteristic nitrosylchloride addition product, melting point 72–73°. Insufficient ether was formed to be isolated but its odor was not that of primary ethyl isoamyl ether. Thus, the addition of hydrogen bromide in aqueous solution proceeds in the so-called normal manner.

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[1] Kondakov, J. Russ. Phys. Chem. Soc., *19*, 300 (1887).

Trimethylethylene.—Part of the trimethylethylene used in the following experiments came from Kahlbaum; part of it was prepared by the catalytic dehydration of dimethylethyl carbinol in the presence of alumina. That this material contained no other olefins except trimethylethylene and methylethylethylene, was shown by its behavior with sulphuric acid (2 volumes of acid + 1 volume of water): both of these olefins dissolve in acid of this concentration.

This hydrocarbon was treated with hydrogen bromide-acetic acid, 100 g. of crude bromide being obtained from 50 g. of olefin. The non-homogeneity of this product was evident from the wide spread in the boiling range, 103–112°. The deficiency in bromine was due to contamination with a small amount of amylene which was difficult to remove.

Anal. Calcd. for $C_5H_{11}Br$: Br, 52.9%. Found: Br, 50.2%, d_0^0, 1.2233.

Repeated treatment with water hydrolyzed 85–90% of the bromide with formation of a tertiary alcohol, dimethylethyl carbinol. The remainder of the bromide did not dissolve in water on long standing or on heating.

The bromide, insoluble in water, was dried and distilled. After removal of olefin, the bromide came over at 110–114°.

Anal. Calcd. for $C_5H_{11}Br$: Br, 52.9%. Found: Br, 50.5%.

This insoluble bromide was refluxed with alcoholic potassium hydroxide; the chief product was a hydrocarbon boiling at 32–36° which was identified as trimethylethylene by the formation of a nitrosylchloride addition product melting at 72–73°.

The above data show that trimethylethylene (containing a small proportion of methylethylethylene) adds hydrogen bromide in two directions. Had the addition been solely in the normal manner, the product would have been a tertiary bromide, which would have reacted with water to form tertiary alcohol and hydrocarbon. Actually, only 85–90% of the hydrogen bromide added normally.

$$(CH_3)_2C{=}CHCH_3 + HBr \rightarrow (CH_3)_2CBrCH_2CH_3 \qquad (I)$$

$$CH_3(C_2H_5)C{=}CH_2 + HBr \rightarrow (CH_3)_2CBrCH_2CH_3 \qquad (II)$$

$$(CH_3)_2C{=}CHCH_3 + HBr \rightarrow (CH_3)_2CHCHBrCH_3 \qquad (III)$$

$$CH_3(C_2H_5)C{=}CH_2 + HBr \rightarrow CH_3(C_2H_5)CHCH_2Br \qquad (IV)$$

The fact that hydrogen bromide adds abnormally to methylethylethylene[1] (equation IV) is not surprising since the same behavior was found in the case of isobutylene. The proof of the same abnormal addition of hydrogen bromide to trimethylethylene (equation III) was the formation of trimethylethylene by the action of alcoholic potassium hydroxide on the product of the addition reaction. A parallel experiment on the reaction of aqueous hydrogen bromide with trimethylethylene showed that addition takes place in one direction only, with formation of tertiary bromide.

Addition of Hydrogen Iodide in Acetic Acid Solution

The acetic acid solution of hydrogen iodide was prepared by the saturation of the acetic acid with hydrogen iodide at 0°, such a solution being dark colored, and viscous. It contains 50–60% of hydrogen iodide and needle-shaped crystals separate on standing.

Propylene does not add hydrogen iodide when treated with this reagent.

The *isobutylene* employed was prepared by the method of Butlerov and also by the catalytic dehydration of isobutyl alcohol. When this olefin was contacted with freshly prepared acetic acid-hydrogen iodide (once 45% of hydrogen iodide, another time 60%), an iodide was readily obtained and in good yield, which after drying, distilled at 97–101°. On long standing with water at ordinary temperature or by a 1½-hour contact with boiling water, the iodide was converted into trimethyl carbinol and isobutylene. Thus, the iodide was homogeneous, and the addition of hydrogen iodide to the isobutylene in acetic acid solution proceeds in the direction predicted by Markovnikov.

Isopropylethylene is converted by 60% hydrogen iodide in acetic acid into iodide in good yield. After drying, this product distilled at 137–139° which is the boiling point of the secondary iodide of methylisopropyl carbinol as found by Vishnegradsky.

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[1] The amount of methylethylethylene in the trimethylethylene was very small.

The iodide did not dissolve in water on long standing which proved the absence of tertiary iodide. In order to test the homogeneity of the product, it was refluxed with alcoholic alkali. The main product was trimethylethylene, ether being formed in very small amount. The hydrocarbon dissolved almost completely [1] in sulphuric acid (2 vols. of conc. acid plus 1 vol. of water) and yielded a crystalline nitrosate, melting point, 72–73°. These data show that the material was pure secondary iodide and that, therefore, hydrogen iodide had added normally.

$$(CH_3)_2CHCH{=}CH_2 + HI \rightarrow (CH_3)_2CHCHICH_3$$

This reaction offers a preparative method for pure secondary iodide and also, by elimination of hydrogen iodide, of *pure trimethylethylene.*

Trimethylethylene dissolves completely in sulphuric acid and adds hydrogen iodide in acetic acid solution to form pure tertiary iodide (b.p., 126–128°), which, in turn, dissolves completely in water with formation of tertiary alcohol.

Thus, the addition of hydrogen iodide in acetic acid solution to olefins proceeds in the same manner whether the medium is acetic acid or water.

Addition of Hydrogen Chloride in Acetic Acid Solution

Hydrogen chloride dissolves in acetic acid at 0° to form a solution containing 18% by weight of the halogen acid. It is inconvenient to use such a solution, and the following procedure was followed in the treatment of isobutylene. Dry isobutylene and hydrogen chloride were passed simultaneously into a previously prepared saturated solution of hydrogen chloride in acetic acid at 0°. In this way, a considerable amount of tertiary butylchloride could be prepared in a relatively short time.

This chloride distilled at 51–60°, only about 2% of the product distilling at 60–145°. The first fraction, according to the boiling point, was tertiary butylchloride, but in order to make sure of this point, we studied its reaction with water.

For this purpose, the chloride was refluxed with water under an excess pressure of 340 mm. of mercury. This excess pressure was obtained by the simple expedient of dipping a tube connected to the top of the reflux condenser under mercury. The gas liberated during the reaction was collected in a gasometer. After the evolution of gas had ceased the reaction products were investigated. It was found that the chloride had completely dissolved with the formation of trimethyl carbinol and a certain amount of isobutylene. The latter was identified through its crystalline nitrosylchloride addition product melting at 96–98°.

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[1] The layer of insoluble hydrocarbon was probably isopropylethylene which indicates the elimination of hydrogen iodide in a manner contrary to the generalization of Markovnikov and Zaitsev.

Although the above data showed that tertiary butylchloride was formed by the addition of hydrogen chloride in acetic acid solution, it was interesting to see the effect of water upon primary isobutylchloride since there was no information on this reaction available in the literature. Primary isobutylchloride was prepared from isobutyl alcohol by the action of phosphorus pentachloride; the product boiled at 60–65°. When the primary chloride was refluxed with water under small pressure it did not dissolve and there was no evolution of gas.

Isobutylene added hydrogen chloride in acetic acid solution to give tertiary chloride as the principal product but there was also a small amount of a higher boiling chloride. This latter substance (b.p., 60–147°) contained 24.95% of chlorine and doubtless was a monochloro derivative of polymerized isobutylene—diisobutylene.

Isopropylethylene, prepared according to the method of Vishnegradsky, and boiling at 21–22°, was treated under various conditions with an acetic acid solution of hydrogen chloride. Reaction took place with difficulty and only a small amount of product was obtained. In order to get this material to react with alcoholic alkali, it had to be heated at 130–140° in a sealed tube. The product was an ether, presumably tertiary isoamyl ethyl ether. This result indicates that the chloride which was subjected to saponification was a secondary chloride and that the addition had taken place according to Markovnikov's rule. A parallel experiment was made on the treatment of primary isoamyl chloride, $(CH_3)_2CHCH_2CH_2Cl$, with alcoholic alkali. The reaction was difficult, but a small amount of primary isoamyl ethyl ether was obtained.

It is generally true in the addition of hydrogen halide acid in acetic solution that hydrogen iodide and hydrogen bromide add much faster than hydrogen chloride, but even more interesting was the discovery that hydrogen iodide and hydrogen chloride add according to Markovnikov's rule whereas hydrogen bromide does not.

In spite of a whole series of experiments carried out with the purpose of finding the reason for this difference in behavior, the cause still remains unknown. It was, however, established that acetic acid is not an indifferent solvent but reacts with the organic bromide product. It is quite possible that acetic acid *catalyzes* the isomerization of tertiary bromide into primary bromide.

It is interesting to note that the extent of the abnormal addition is different for different hydrocarbons. The greater the difference in the degree of hydrogenation of the two carbons attached to the double bond, the less is the abnormal reaction, and with diminishing difference in hydrogenation, the relative extent of the two reactions approaches equality.

Thus, with isobutylene, $(CH_3)_2C{=}CH_2$, the abnormal reaction accounts for only 6–7% of the total addition. But for trimethylethylene, $(CH_3)_2C{=}CHCH_2$, the amount of the abnormal reaction is 10–15%, and for isopropylethylene, which has the structure $(CH_3)_2{-}CHCH{=}CH_2$, the yield of abnormal product is 50% of the total product.

ISOMERIZATION OF ISOPROPYLETHYLENE

The first experiments carried out with the idea of learning the reason for the formation of abnormal products in the catalytic decomposition of alcohol were made with amylene which had been prepared from the iodide of fermentation amyl alcohol by the action of alcoholic alkali.

As it is known, this amylene contains only isopropylethylene and unsym-methylethylethylene. Such an amylene boils at 23–28° and does not yield a crystalline nitrosylchloride or nitrosate with nitrosylchloride. A sample of this hydrocarbon (77 g.) was passed through a copper tube filled with ignited alumina during 40 minutes, the catalyst temperature being 540–560°. The experimental conditions were such that only a small amount of amylene was decomposed into gas and it was expected that the molecules of amylene, being near decomposition conditions, would rearrange into the most stable form. Sixty-two grams of hydrocarbon condensed in the receiver, the boiling point being 29–39°; 2–3 g. of residue remained in the distillation flask. The reaction produced 6 liters of gas which contained 38% of C_nH_{2n} and 62% of C_nH_{2n+2}

The hydrocarbon (b.p., 29–39°) was treated with a mixture of acetic acid, amyl nitrate, and nitric acid, and a crystalline product was obtained which melted at 95–96° and which was identified as the nitrosate of trimethylethylene.

The decided change in boiling point and the formation of trimethylethylene nitrosate indicates that isomerization had occurred, probably the conversion of isopropylethylene into its isomer, trimethylethylene.

In order to be sure that isomerization of isopropylethylene had taken place and also that alumina was the catalyst for this rearrangement, a series of experiments was made with pure isopropylethylene. The latter was prepared by the procedure of Vishnegradsky and also by the catalytic method. It was found that isopropylethylene yields very small amounts of trimethylethylene when passed through an empty glass tube. Thus, at 400–500°, only traces of trimethylethylene were found, and when the feed rate was 25 g. per hour and the temperature 530–540°, the product was a hydrocarbon boiling at 23–33° which formed a certain amount of crystalline nitrosate, but the yield of trimethylethylene was still very small. Thirty-eight grams of isopropylethylene was passed at 600° through a glass tube during 35 minutes; there was considerable decomposition, 8 liters of gases being obtained. Nineteen grams of hydrocarbon condensed in the receiver, of which 10 grams distilled at 23–39°, the remaining amount representing polymerization products.

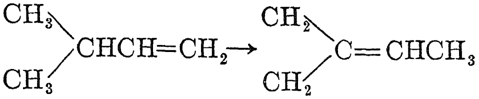
The hydrocarbon formed a crystalline nitrosate and on treatment with sulphuric acid (2 vols. of acid plus 1 vol. of water), about 10% of the hydrocarbon dissolved. These data show that it is possible to isomerize isopropylethylene into trimethylethylene by the action of heat alone, but only to a small extent. There was scarcely any carbon deposition in the tube. The composition of the gas was as follows:

$$C_nH_{2n},\ 46.3\%;\ H_2,\ 3\%;\ C_nH_{2n+2},\ 50.5\%$$

The behavior of isopropylethylene is quite different in the presence of ignited alumina in either a glass or a copper tube. Isomerization becomes active at 450° and at this temperature there is practically no liberation of gas. Thus, a yield of 35 g. of hydrocarbon boiling at 30–39° was obtained from 38 g. of isopropylethylene. This product contained at least 60% of trimethylethylene, the remaining 40% being unchanged isopropylethylene. From the product was obtained a crystalline nitrosate melting at 96–97°.

Forty grams of isopropylethylene was passed over alumina at 525° in a copper tube during two hours; 33 g. of liquid product was obtained, boiling point 30–39°, which contained about 80% of trimethylethylene. Also 1.5 liters of gas was obtained.

Thus, the presence of alumina promotes the conversion of isopropylethylene into trimethylethylene



$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CHCH{=}CH_2 \rightarrow \left.\begin{matrix}CH_2\\CH_2\end{matrix}\right\rangle C{=}CHCH_3$$

and since its action is purely catalytic, such a conversion of one organic compound into another, isomeric with it, must be called *catalytic isomerization.*

After the fact of the conversion of isopropylethylene into trimethylethylene under the influence of alumina had been established the next interesting point was the question whether or not this isomerization was reversible, i.e., was the same catalyst able to convert trimethylethylene back into isopropylethylene. Several experiments were made with this purpose in mind. No certain conclusion was possible but it is probable that alumina is not able to reverse the isomerization. However, there was a certain amount of reaction and a product was obtained the structure of which we were not able to establish. The trimethylethylene taken for these experiments dissolved in sulphuric acid (2 parts by weight of acid and 1 part of water), and with an acetic acid solution of hydrogen iodide it gave an iodide boiling at 120–124°.

Thirty-nine grams of trimethylethylene boiling at 36–39° was passed over alumina at 520–530° in a copper tube during 80 minutes; 36 g. of product was obtained with a boiling range of 30 to 42°, 10 g. boiling at 30–35°. About 85% of this material dissolved in sulphuric acid (2 parts by weight of acid and 1 part of water) and it reacted with hydrogen iodide in acetic acid to give an iodide boiling at 120–121°. (It should be remembered that we had shown that hydrogen iodide adds in the normal manner.) In another experiment, 100 g. of trimethylethylene was passed over alumina at 540–550° in a copper tube, the duration of the experiment being

160 minutes. The products were 85 g. of hydrocarbon liquid and 7 liters of gas. The boiling point of the liquid was 29–41°, 55 g. distilling at 29–38° and 15 g. at 38–41°.

Fifty cc. of the hydrocarbon was shaken with sulphuric acid (2 parts by weight of acid and 1 part of water) and another 25 cc. of the hydrocarbon was shaken with sulphuric acid made from 2 volumes of acid and 1 volume of water. There remained, insoluble in these concentrations of acid, 9 g. of the hydrocarbon, boiling point 28–38°. Repeated treatment with a mixture of 2 volumes of sulphuric acid and 1 volume of water failed to have any effect upon it except to change its boiling point (after the second treatment to 28–32°). We did not succeed in establishing the structure of this material but from the data at hand we should not consider it to be isopropylethylene.

Unfortunately, I did not publish information on the behavior of this material, which boiled at 28–32°, with permanganate. If it should be stable to permanganate, it must be a saturated hydrocarbon, e.g., isopentane, and its formation can be explained by the same hypothesis that I have proposed in the case of polymerization and dehydration. (See chapter on "Theoretical Principles of Catalytic Reactions.")

Isopropylethylene is converted into trimethylethylene when the former is passed over ignited alumina at 500–505° in a copper tube. The product forms a crystalline nitrosate melting at 96–98° and boils at 26–38°. Treatment with sulphuric acid (2 vols. of acid and 1 vol. of water) showed that it contained about 45% of trimethylethylene. Likewise, the same isomerization takes place under the combined effect of alumina and high pressure at 480°. The product from this experiment boiled at 25–41°, gave the characteristic nitrosate of trimethylethylene, and dissolved, for the greater part, in sulphuric acid. But there was also another product, diamylene, since amylene polymerizes readily under these conditions.

After these experiments with isopropylethylene it becomes clear why trimethylethylene is formed when amyl alcohol vapor is contacted with alumina; it is due to the catalytic isomerization of the normal dehydration product, isopropylethylene. However, before discussing the theoretical aspects of the formation of trimethylethylene through the action of zinc chloride and sulphuric acid, I shall first describe some experiments on the butylenes.

ISOMERIZATION OF BUTYLENES

Preceding experiments had shown that the catalytic decomposition of isobutyl alcohol in the presence of alumina yields only isobutylene and we can assume, therefore, that water is eliminated in one direction only. In order to determine the effect of alumina and high temperature upon isobutylene, this olefin was passed over alumina at temperatures up to 500–600°. In one experiment, isobutylene prepared by the action of alcoholic alkali upon isobutyl iodide, was passed through a glass tube containing pieces of graphite crucible at 500°, the gas speed being 3 liters per hour. The gas obtained had the following composition:

$$C_nH_{2n}, 70\%; H_2, 15.8\%; C_nH_{2n+2}, 14.2\%$$

The iodide formed by passing the gas through aqueous hydrogen iodide boiled at 97–101° and readily dissolved in water. Consequently, the iodide was tertiary and the parent olefin was pure isobutylene.

The non-absorbed gas contained saturated and also unsaturated hydrocarbons and the latter reacted with bromine water to yield a bromide boiling at 140–143° which was shown to be propylene bromide. Therefore, isobutylene, under the conditions of the experiment, splits to a certain extent into propylene.

It is also possible that there is a preliminary polymerization of isobutylene to diisobutylene which subsequently splits into propylene and saturated hydrocarbons.

$$2C_4H_8 \rightarrow C_8H_{16}$$
$$C_8H_{16} \rightarrow C_2H_6 + 2C_3H_6 + 2H_2$$

In another experiment, 20 liters of isobutylene was passed over the above catalyst during five hours at 550–600° and there was no evidence of the formation of isomeric butylenes.

These experiments were made before it was realized that isopropylethylene is converted into trimethylethylene under the influence of catalysts. We showed that the structure, $CH{=}CH_2$, can be changed into $C{=}CH$, which contains a tertiary carbon atom. Now, in isobutylene we already have the structure $C{=}CH_2$ and our experiments show that this cannot be changed into $CH{=}CH$, which is characteristic of β-butylene. At the present time, after studying polymerization, it is understandable why this is so. (See chapter on the "Theoretical Principles of Catalytic Reactions: Polymerization.")

But it is well known that isobutylene obtained by the action of molten zinc chloride upon isobutyl alcohol contains, beside isobutylene, also a considerable amount of other butylenes. It was interesting to determine the cause of these abnormal products and also to study the influence of temperature upon the relative amounts of the various butylenes obtained. The last named problem had especial interest because Nef[1] had obtained pure isobutylene by heating isobutyl alcohol in a glass flask at 400–450°. The usual procedure for the decomposition of isobutyl alcohol with zinc chloride had been to heat the chloride in a red hot iron vessel and to add the alcohol from a funnel. The evolved gas contained much hydrogen and saturated hydrocarbons and the liquid contained, among other things, isobutyric aldehyde. It is not possible to decide which catalyst was responsible for the aldehyde—it is well known that iron could promote its formation. It was assumed that the butylene was formed by virtue of the ability of zinc chloride to remove water from the alcohol. In order to avoid contact with iron, the zinc chloride was placed in a copper tube heated electrically.

Experiments on the decomposition of isobutanol[2] were carried out at temperatures of 540–560° and 360–370°.

At 550–560°, 190 g. of alcohol produced 42 liters of gas and about 50 g. of isobutyric aldehyde. The duration of the heating was 95 minutes. Analysis of the gas gave the following results:

CO_2, 0.8%; C_nH_{2n}, 37.7%; CO, 1.6%; H_2, 51.0%; C_nH_{2n+2}, 7.2%

At 540–550°, and with a faster alcohol feed, a slightly smaller amount of gas was obtained, the analysis of which gave the following results:

C_nH_{2n}, 47.2%; CO, 2%; H_2, 43.8%; C_nH_{2n+2}, 6.4%

This gas was passed through an acetic acid solution of hydrogen iodide, and an iodide was obtained which boiled at 103–116°. When this iodide was heated with water, a secondary iodide was separated, boiling point, 115–118°.

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[1] Nef, Ann., *318*, 213 (1901).

[2] Mr. Kostin participated in the experiments on the decomposition of isobutanol by zinc chloride.

About 25% of the total iodide was secondary. Decomposition of the secondary iodide with alcoholic alkali yielded β-butylene which did not form a crystalline nitrosate. In order to determine the effect of temperature upon the formation of β-butylene, another experiment on the decomposition of isobutanol was made with zinc chloride at 360–370°. Two hundred and forty-eight grams of alcohol was passed over the catalyst during 110 minutes and 19 liters of gas was obtained which contained 78.8% of unsaturates, traces of carbon monoxide, and 20% of hydrogen and saturates.

The gas reacted with an acetic acid solution of hydrogen iodide with the formation of 91 g. of iodide boiling at 102–118°. Two treatments of this crude iodide with hot water separated 23 g. of insoluble secondary iodide corresponding to about 25% of the total iodide. Analytical figures pointed to the composition C_4H_9I for the secondary iodide; analysis giving 68.4% iodine, the theory demanding 69.0%. In the liquid product there was considerable isobutyric aldehyde.

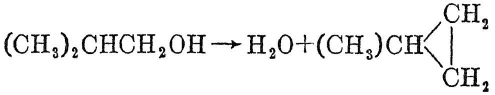
Thus, at the temperatures studied, the relative amounts of iso- and β-butylenes remained the same. Zinc chloride behaves differently from alumina. With the former, two reactions take place, *dehydration* and *dehydrogenation*, the latter reaction resulting in the aldehyde decomposition of the alcohol. Probably the dehydrogenation reaction is promoted by a small amount of oxide or free metal formed by the action of hydrogen and carbon upon the chloride. This would be an example of *autocatalysis*. It was observed that the yield of butylene increased and the formation of hydrogen decreased with diminishing temperature of decomposition.

Finally, in order to determine the effect of zinc chloride upon pure isobutylene, this gas was passed through a copper tube containing zinc chloride at 600°, 14 liters of olefin being passed during 6 hours. Analysis of the gas showed the presence of 72–78% of unsaturated hydrocarbons. Treatment of the gas with hydrogen iodide in acetic acid gave an iodide boiling at 98–104°, and when this product was heated with water, only 0.5 g. of liquid remained undissolved, scarcely enough for the determination of its structure. This experiment showed that zinc chloride is not able to catalyze the conversion of iso- into β-butylene. Likewise, other experiments showed that β-butylene is not transformed into isobutylene by the action of catalysts.

If this is true, then how is the formation of α- and β-butylenes by the action of zinc chloride upon isobutanol to be explained? The simplest assumption is that zinc chloride promotes the elimination of water in different directions similar to the effect of alcoholic alkali upon alkyl halides. The so-called normal elimination of water consists in the removal of the elements of water from adjacent carbon atoms (I); the abnormal elimination when the hydroxyl group and the hydrogen atom comes from non-adjacent carbons (II). In the former case an open chain olefin results; in the latter, a closed chain.

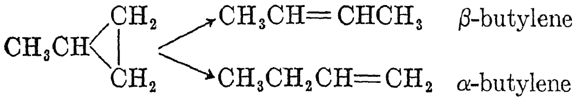
$$\text{(I)}\quad (CH_3)_2CHCH_2OH \rightarrow H_2O + (CH_3)_2C{=}CH_2$$

(II)



$$(CH_3)_2CHCH_2OH \rightarrow H_2O + (CH_3)CH\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}$$

Cyclic paraffin hydrocarbons (naphthenes) readily undergo catalytic isomerization into open chain olefins, especially cyclopropanes, as shown by my experiments and also those of Huhn.



In such a way might be explained the formation of alpha- and beta-butylenes from isobutyl alcohol, in the presence of various catalysts. This hypothesis explains the formation of abnormal products from fermentation amyl alcohol although, of course, catalytic isomerization may take place at the same time. Likewise, the formation of a number of products when primary isobutyl chloride is passed through a heated tube may be explained by the removal of hydrogen halide acid from different positions.[1]

Another question arises: Why is only isobutylene produced by the catalytic dehydration of isobutyl alcohol by alumina? Consideration of the available data on the production of olefins by the dehydration of alcohols shows that strong dehydrating agents such as zinc chloride, sulphuric acid, and phosphorus pentoxide always produce a mixture of olefins. Such an active agent promotes the removal of water in such a manner that the greatest amount of free energy is liberated. The alumina, on the other hand, is an inert substance and functions only when a large amount of energy is applied, and water is eliminated in such a way that the hydroxyl group combines with the least stable hydrogen atom.

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[1] Nef, Ann., *318*, 211 (1901).

In order to investigate the removal of water from secondary butyl alcohol I made the following experiments with Zdzitovesky. Methylethyl carbinol, synthesized according to the method of Wagner from acetaldehyde and zinc ethyl, was passed over alumina in a copper tube at 440–450°. Seventy-five grams of alcohol gave 11.6 liters of gas which analyzed for pure butylene. This gas was treated with nitrosyl chloride and with hydrogen iodide in order to see if it contained isobutylene. Nitrosyl chloride gave a very small amount of nitrosyl chloride addition product melting at 104–105°, but the corresponding derivative of isobutylene has the melting point of 98°. The reaction with hydrogen iodide also indicated the absence of isobutylene.

There was some doubt as to the purity of the methylethyl carbinol, there being the possibility of contamination by trimethyl carbinol. The iodide obtained from the alcohol by the action of iodine and phosphorus boiled at 115–121° and contained the percentage of halogen corresponding to C_4H_9I. When this iodide was heated with water a part of it dissolved, and the product, separated from the water layer by the addition of potash, had the odor of a tertiary alcohol. Methylethyl carbinol was then prepared by another method, the catalytic hydrogenation of methylethyl ketone under high pressure in the presence of nickel oxide. (See chapter on "Hydrogenation.") This alcohol was very pure and was obtained in excellent yield. Phosphorus and iodine gave an iodide boiling at 117–120°. One hundred and forty grams of this iodide was heated with 280 g. of water for three hours. According to Sheshukov,[1] secondary butyl iodide does not dissolve in water under these conditions. This iodide, however, dissolved, but much slower than the tertiary iodide and more water was necessary. After the first treatment 117 g. remained; after the second treatment, 72 g.; after the third, 47 g.; after the fourth, 30 g.; all the iodide had disappeared after the fifth treatment. A secondary butyl alcohol separated from the water, which, as shown by the test with Denijes' reagent (solution of mercuric oxide in sulphuric acid) was free from tertiary alcohol. Two facts were proved by these experiments—secondary butyl iodide dissolves in water and the methylethyl carbinol used in this investigation was free from trimethyl carbinol.

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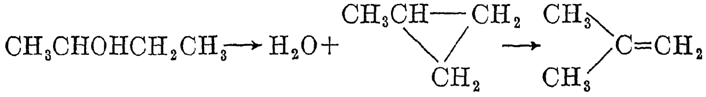
[1] Sheshukov, J. Russ. Phys. Chem. Soc., *18*, 211 (1886).

β-butylene was prepared by passing this pure secondary butyl alcohol over alumina at 450° in a copper tube; the alcohol was almost completely decomposed into butylene and water.

The alcohol undecomposed by Denijes' reagent was found to contain a trace of isobutylene. In order to determine whether or not isobutylene was present in the butylene resulting from the dehydration of secondary butyl alcohol, the gaseous product was treated with aqueous hydrogen iodide, and the iodide was decomposed by water. However, only traces of isobutylene were found in the gas, and then only by Denijes' reagent. The simplest explanation of the presence of traces of isobutylene being formed from methylethyl carbinol would be the primary formation of a cyclic hydrocarbon which would easily isomerize into an open chain olefin in the presence of alumina.



Under the above conditions of dehydration, this side reaction takes place only to a small extent. However, when methylethyl carbinol is passed through a copper tube at 450° over zinc chloride, the butylene product contains a large proportion of isobutylene as well as some methylethyl ketone and an unsaturated liquid hydrocarbon.[1] Concerning the formation of olefins containing double the number of carbon atoms [2] as the original alcohol, I would say that they result not only through simple polymerization of the olefins formed by the dehydration of the alcohols, but they can be formed through the intermediary of the ethers, which are the first step in the dehydration of alcohols.

$$2C_3H_7CH_2OH—H_2O \rightarrow C_3H_7CH_2OCH_2C_3H_7$$

$$C_3H_7CH_2OCH_2C_3H_7 \rightarrow H_2O + C_3H_7CH{=}CHC_3H_7$$

The ether may decompose into water and two molecules of olefin or into water and one molecule of an olefin with twice the number of carbon atoms. The formation of butadiene, $CH_2{=}CHCH{=}CH_2$, from ethanol in the presence of strongly ignited alumina and powdered aluminum, is evidence for this mechanism and also the observation made by me on the formation of ethers by passing alcohols over zinc chloride, the same as in the case of alumina. Thus, it may be considered that alumina promotes only the formation of β-butylene from secondary butyl alcohol, but that with stronger dehydrating agents, there is an increase in abnormal reaction due to the elimination of water from other positions and subsequent rearrangement of the first formed cyclic compound into isobutylene.

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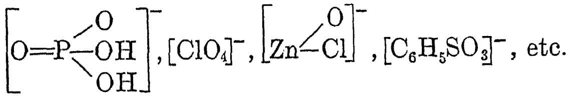
[1] Ipatieff, J. Russ. Phys. Chem. Soc., *35*, 592 (1903).

[2] Favorsky, *ibid.*, *35*, 543 (1903).

ISOMERIZATION OF NORMAL BUTENES[1] IN THE PRESENCE OF PHOSPHORIC ACID

The rearrangement of normal butenes in the presence of catalysts has not been studied quantitatively previously. Gillet [2] found that 1-butene changes into 2-butene when passed over heated aluminum sulphate. According to Hurd [3] such rearrangement also occurred during pyrolysis, with the ratio of the lower boiling 2-butene (0.5°) to the higher boiling 2-butene (2.5°) being 3/2. Runge and Mueller-Cunradi [4] patented a method of converting 1- into 2-butene by heating to 400–600° in an empty quartz tube or at 420° in contact with lime, aluminum phosphate, pumice, or bauxite.

The present chapter deals with rearrangements of normal butenes in the presence of catalysts. It is here assumed that the isomerization reaction consists of two steps: (1) formation of an addition product of the olefin with the catalyst and (2) the decomposition of such addition product whereby the same olefin or one with a different structure is split off and the catalyst is regenerated. In the following equations illustrating the isomerization, "A" represents groups such as



$$\left[O{=}P\begin{matrix}{\diagup}O\\ -OH\\ {\diagdown}OH\end{matrix}\right]^-, [ClO_4]^-, \left[Zn\begin{matrix}{\diagup}O\\ -Cl\end{matrix}\right]^-, [C_6H_5SO_3]^-, \text{etc.}$$

$$CH_3CH_2CH{=}CH_2 + HA \rightarrow$$

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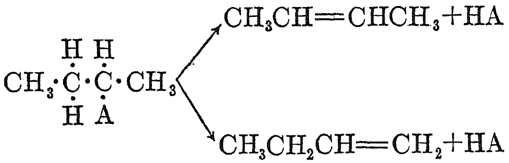
[1] Ipatieff, Pines, and Schaad, J. Am. Chem. Soc., *56*, 2696 (1934).

[2] Gillet, Bull. soc. chim. Belg., *29*, 192 (1920).

[3] Hurd, Ind. Eng. Chem., *26*, 51 (1934); Hurd and Goldsby, J. Am. Chem. Soc., *56*, 1812 (1934).

[4] Runge and Mueller-Cunradi, U.S. Patent, 1,914,674, June 20, 1933; C.A., *27*, 4353 (1933).



$$\mathrm{CH_3\cdot\underset{H}{\overset{H}{C}}\cdot\underset{A}{\overset{H}{C}}\cdot CH_3}\begin{cases}\nearrow \mathrm{CH_3CH{=}CHCH_3+HA}\\ \searrow \mathrm{CH_3CH_2CH{=}CH_2+HA}\end{cases}$$

Experimental Part

Apparatus and Procedure.—The apparatus used (Fig. 17) for studying isomerization of butenes at ordinary pressure consisted of two 2-liter gas burets, two leveling flasks, and a U-shaped reaction tube one-third full of glass spheres (3 to 5 mm. diameter) and surrounded by a jacket in which water and organic liquids were refluxed to maintain chosen, constant temperatures. The butene under investigation contained in the left buret was passed at a rate of 400–450 ml. per hour through a weighed quantity of the liquid isomerizing catalyst in the U-reaction tube and collected in the other buret which was always kept at approximately atmospheric pressure by manipulation of the leveling flasks.

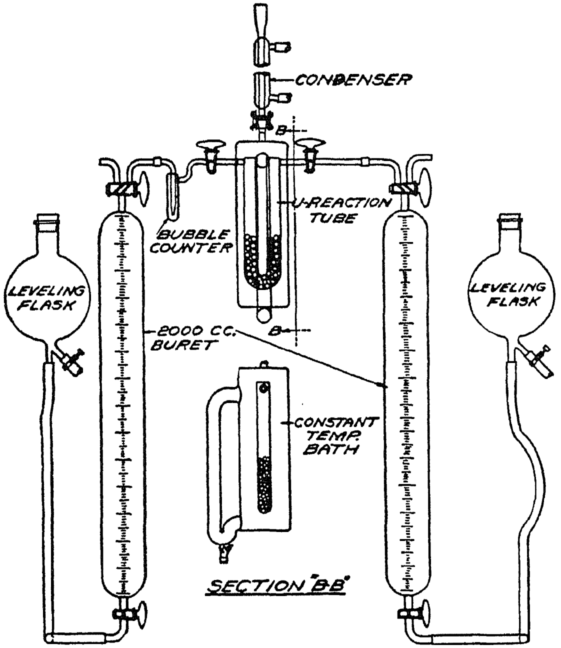


Fig. 17

For the experiments at superatmospheric pressure, the liquid butene under the desired nitrogen pressure in a steel charger provided with a gage glass, was passed through small copper tubing to the steel tube (13 mm. inside diameter) containing the solid catalyst. The speed of the butene flow was controlled by a needle valve at the exit end of the catalyst tube and a calibrated flowmeter through which the treated gas passed before collection over salt water in a calibrated gas holder, or, in some cases, liquefaction in a trap kept at −78° by solid carbon dioxide and acetone.

Method of Analysis.—The butene after subjection to the action of a catalyst under either atmospheric or higher pressure was analyzed by Podbielniak's [1] low-temperature fractional distillation method—the normal boiling points of the normal butenes being: 1-butene, −5.0°; *cis*-2-butene, +0.5°; and *trans*-2-butene, +2.5°.

Preparation of the Butenes.—Dehydration of 1-butanol (0.5 mole per hour) over activated alumina at 427° gave 1-butene (100% pure), a result checking that of Pines.[2] However, after intermittent use in preparing several liters of liquefied butenes, the activated alumina then produced mixtures of 1- and 2-butene containing approximately 6% of the latter. Such partial isomerization is thought to be due to accumulation on the catalyst of small amounts of acidic materials resulting from oxidation by traces of air accidentally entering the catalyst chamber during shut-down periods.

The *trans*-2-butene was separated by low-temperature fractional distillation from a butene mixture (14.1% 1-C_4H_8, 8.2% *cis*- and 77.7% *trans*-2-butene) prepared by dehydrating 2-butanol at 300% over diatomaceous earth impregnated with phosphoric acid.

Other mixtures containing 65 to 88% of 2-butene were prepared similarly from 1-butanol, a result in agreement with that of Komarewsky and Johnstone [3] but contradicting that of King,[4] who reported the formation of 2-butene only by passing 1-butanol over pumice impregnated with glacial phosphoric acid.

Since exposure to sunlight is known to cause rearrangement of certain bromoalkenes (BrCH=CHBr and CH_3CH=CHBr)[5] into equilibrium mixtures of the *cis*- and *trans*-isomers, it was desired to see whether *trans*-2-butene undergoes any such change. Accordingly the whole fraction, shown by analysis to be pure *trans*-2-butene, was then divided into three parts and stored as follows: (1) in a brown bottle kept in the dark at room temperature, (2) in a bottle of ordinary glass exposed to light, and (3) in the liquid phase at −78°. After such storage for twelve days, all three samples were analyzed again and found to be pure *trans*-2-butene, which was saved for the experiment with phosphoric acid.

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[1] Podbielniak, Ind. Eng. Chem., Anal. Ed., *5*, 172 (1933).

[2] Pines, J. Am. Chem. Soc., *55*, 3892 (1933).

[3] Komarewsky and Johnstone, private communication.

[4] King, J. Chem. Soc., *115*, 1404 (1919).

[5] Van de Walle, Bull. soc. chim. Belg., *27*, 209 (1913).

Discussion of Results

Isomerization of 1-Butene in the Presence of Phosphoric Acid.—As the temperature was raised, increasing amounts of 1-butene isomerized into 2-butene by passing through 36 g. of 100% orthophosphoric acid in the apparatus shown by Fig. 1. Between 3 and 6% by volume of butene was absorbed.

Mixtures containing 20 to 30% of 1-butene and 70–80% 2-butene resulted when either 1-butanol or 1-butene passed at a rate of 1 mole per hour through a Pyrex tube heated to 427° and packed with a 60 cc. gross volume of granular solid prepared from hydrate of alumina (1 mole) and orthophosphoric acid (1.6 moles).

TABLE 36

ISOMERIZATION OF 1-BUTENE BY 100% ORTHOPHOSPHORIC ACID

Temp., °C.		26	78	100	135
% By Volume	1-C_4H_8	96	88	66	40
	2-C_4H_8	4	12	34	60

Similar increase in isomerization with temperature rise (compare Table 36) was observed under pressure in the presence of diatomaceous earth impregnated with phosphoric acid (Table 37). At 249° this material converted 1-butene quantitatively into 2-butene without formation of polymers, but when the experiment was continued for a long time at 250 to 325°, this solid lost part of its activity as evidenced by the fact that isomerization to the 2-isomer was then 70 to 80% complete. Perhaps the decrease in isomerization activity was due to a slow partial dehydration of orthophosphoric acid through the pyro- and toward metaphosphoric acid.

With the second sample of the diatomaceous earth-phosphoric acid mixture, evidence of equilibrium was observed in that increasing the contact time about four-fold made no change in the percentage conversion of 1- into 2-butene. With contact times of 205 to 270 and 1020 seconds, from 72 to 79% of 2-butene was formed.

TABLE 37

ISOMERIZATION OF 1-BUTENE UNDER PRESSURE IN THE PRESENCE OF DIATOMACEOUS EARTH IMPREGNATED WITH PHOSPHORIC ACID

SAMPLE NO. 1 CATALYST "D"			TIME, HRS.	C_4H_8 EXIT RATE, l./HR.	EXIT C_4H_8, % BY VOLUME		CONTACT TIME, SEC.
Period No.	T., ° C.	Press., Atms.			1- C_4H_8	2- C_4H_8	
			Butene charged		94	6	
1	100	2.45	4.25	3.6	64	36	83
2	99	6.0	5.00	4.0	79	21	244
3	126	7.8	4.25	3.5	26	74	255
4	149	7.8	5.00	3.7	16	84	226
5	174	7.9	3.75	3.3			243
6	200	7.8	2.50	3.6	5.5	94.5	208
7	249	7.8	2.75	3.3	0.0	100.0	206

Isomerization of 1-Butene in the Presence of Other Substances.—Further experiments at atmospheric pressure (Fig. 1) showed formation of 2-butene to be: 21% at 21° in the presence of perchloric acid (70–72%); 13% at 76° in the presence of benzene sulphonic acid (75% aqueous solution); 5% at 100° in the presence of an aqueous solution containing 75% of zinc chloride. Glacial acetic, mono- and dichloro acetic acids caused no isomerization at 100°.

Isomerization of trans-2-Butene by Phosphoric Acid.—Pure *trans*-2-butene (450 cc. per hour) on passage through 36 g. of 100% orthophosphoric acid at 100° (Fig. 1) underwent partial isomerization to a mixture containing 6.6% 1-butene, 6.0% *cis*- and 87.4% *trans*-2-butene.

Summary

(1) Isomerization of 1- into 2-butene was slight in the presence of phosphoric acid at room temperature and increased with rising temperature. A similar increase in isomerization of 1- into 2-butene with temperature rise was observed under pressure in the presence of diatomaceous earth impregnated with phosphoric acid. At 249° isomerization was complete under 7.8 atmospheres pressure.

(2) Pure *trans*-2-butene underwent partial isomerization into

1-butene (6.6%) and *cis*-2-butene (6.0%) during passage through 100% orthophosphoric acid at 100°.

(3) 1-Butene isomerized partially into the 2-isomer in the presence of perchloric acid and aqueous solutions of zinc chloride and benzene sulphonic acid.

CATALYTIC ISOMERIZATION OF CYCLIC PARAFFINS

In order to clarify the manner of formation of abnormal products in the decomposition of isobutyl alcohol in the presence of various dehydrating agents, it was first necessary to investigate the decomposition conditions of cyclic polymethylene hydrocarbons which are the intermediate products and it also seemed desirable to study the effect of various catalysts upon the opening of closed chains. The first experiments on the decomposition of cyclic hydrocarbons, carried out with the coöperation of Huhn,[1] were made in glass tubes. Previously, it had been demonstrated by Tanatar [2] that the cyclopropane ring was opened with resultant formation of propylene when the cyclic hydrocarbon was passed through a heated glass tube. This finding was contradicted by Volkov and Menshutkin,[3] who showed that pure cyclopropane is unchanged under the experimental conditions employed by Tanatar and that it is decomposed only at high temperature, and then, not into propylene, but into ethylene, the propylene found by Tanatar being an impurity in the starting material. However, Tanatar repeated his experiments with the necessary experimental precautions and verified his original conclusion. Since this question was very important for me, I also repeated this work. The cyclopropane was shaken with 2% permanganate solution for one week, and was then passed in the dark through bromine water containing excess bromine, and finally collected over 2% permanganate. This gas did not decolorize permanganate solution. The dry gas, free from oxygen, was bubbled through strong potassium hydroxide solution and then passed over iron filings at 600° contained in a glass tube; the exit gas was collected over water. The exit gas contained 50–70% of propylene as determined by oxidation with permanganate and also by conversion into dibromide, the latter being pure propylene dibromide, boiling point 141–142°.

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[1] Ipatieff and Huhn, Ber., *36*, 2014 (1903).

[2] Tanatar, Ber., *29*, 1927 (1896); *32*, 802 (1899).

[3] Volkov and Menshutkin, Ber., *31*, 3067 (1898).

The gas remaining after the absorption of propylene by bromine was shown by analysis to be unchanged cyclopropane. Thus, it is quite certain that 600° cyclopropane is converted into propylene and we would expect the same isomerization to take place even more readily in the case of methyl cyclopropane.

Tanatar [1] also investigated the catalytic action of platinum black upon cyclopropane in a sealed tube at ordinary temperature and at 100° in the presence of moisture and air, conversion into propylene being evident at both temperatures. The reaction rate is doubtless influenced by the presence of moisture. We studied the behavior of dry cyclopropane at ordinary pressure, in the presence of both platinum black and alumina.

Catalytic Isomerization of Cyclopropane

The cyclopropane, prepared according to the method of Gustavson, was purified by shaking with a 2% solution of potassium permanganate. After drying with calcium chloride and potassium hydroxide the gas was passed with extreme slowness through a small tube containing platinum black or alumina, the tube being heated in the usual manner. To determine the amount of propylene formed, a definite volume of the resulting gas was treated in a graduated cylinder with potassium permanganate solution (a tube with solid potassium permanganate was introduced into the cylinder), and the propylene content was calculated from the diminution in volume.

The platinum black catalyst was prepared according to the method of Levy.[2] Seven hundred cc. of gas was passed at 200° over the catalyst during 90 minutes and 4 to 5% of it was converted into propylene. In another experiment, 500 cc. of cyclopropane was passed through a tube containing 2 g. of platinum black at 315° during 105 minutes; the percentage conversion into propylene was about 29%. In the absence of catalyst at 370° and at a very slow feed rate (700 cc. in 195 minutes), cyclopropane was isomerized into propylene to the extent of 1 to 2% whereas at a considerably faster feed rate, cyclopropane was isomerized into propylene by alumina at 350–360° to the extent of 15 to 20%. These experiments establish, without doubt, the fact of the catalytic isomerization of cyclopropane into propylene.

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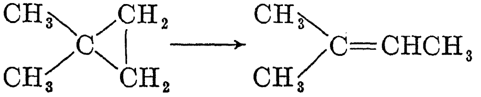
[1] Tanatar, Z. physik. Chem., *41*, 735 (1902).

[2] Levy, Ber., *23*, 289 (1890).

Unsym-dimethylcyclopropane was prepared by the procedure of Gustavson and Popper[1] from the bromide of pentamethylene glycol by treatment with zinc dust and 75% alcohol, the pentamethylene glycol having been synthesized according to the method of Tollens and Apel.[2] The resulting unsym-dimethylcyclopropane distilled without residue at 21–22° and did not immediately decolorize 1% permanganate solution. It was passed through a glass tube containing alumina at 340–345° at a feed rate of 8 g. of hydrocarbon in 71 minutes. No gas was liberated; 7.5 g. of hydrocarbon collected in the receiver, the boiling range of which was 36–37°, distillation starting at 35°. That this substance was *trimethylethylene* was indicated by its boiling point and by its ability to combine with bromine and to immediately decolorize 1% permanganate solution. Further evidence was obtained through the preparation of its nitrosate by means of nitric acid and amyl nitrate. The melting point of the nitrosate was 97–98°, and analysis showed a nitrogen content of 17.33% as compared with 17.28% calculated for $C_5H_{10}N_2O_4$. Molecular weight determination (boiling point method in benzene) gave the value 153 as compared with the theoretical 162.

Thus, in the presence of alumina, the transformation of dimethylcyclopropane into trimethylethylene takes place at relatively low temperature.



This work was not repeated in the absence of catalyst due to lack of material.

Catalytic Isomerization of Cyclohexane

Cyclohexane was heated at 450° in the Ipatieff bomb in the presence of alumina. A considerable portion of the product boiled at 69–73°.[3]

Anal. Calcd. for C_6H_{12}: C, 85.7%; H, 14.3%. Found: C, 85.8%; H, 14.1%; d_0^{20}, 0.7518; n_D, 1.4093; M.R., 27.64.

These values compare favorably with those of methylcyclopentane, as determined by Kischner[1] (b.p., 71–73°; d_0^{20}, 0.7498; n_D, 1.4101) who accomplished the conversion of cyclohexane into methylcyclopentane by heating the former with hydriodic acid in a sealed glass tube. Thus, it is seen that alumina also promotes this isomerization:

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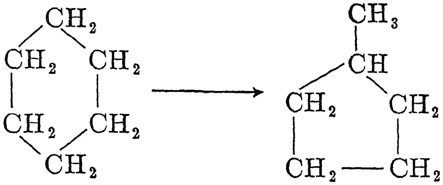
[1] Gustavson and Popper, J. prakt. Chem., *58*, 458 (1898).

[2] Tollens and Apel, Ann., *289*, 36 (1895).

[3] Ipatieff and Dovgolevitsch, Ber., *44*, 2987 (1911).



In order to establish more rigorously the structure of the hydrocarbon fraction boiling at 69–73°, it was nitrated according to the procedure of Konovalov. Eight sealed tubes, each containing 2 cc. of hydrocarbon and 12 cc. of nitric acid (*d*, 1.08) were heated in an oil bath for 24 hours at 120°. The dark colored hydrocarbon layer was washed with sodium carbonate solution, dried, and distilled. After distilling off the unreacted material, a fraction was collected at 179–181° which was shown to be a tertiary nitro compound since the test of Konovalov with potassium hydroxide for the primary and secondary nitro groups gave negative results. The non-nitrated material was unchanged methylcyclopentane since it distilled at 70–74° and had the density of d_0^{20} 0.7551.

An attempt to isomerize cyclohexane into methylcyclopentane under ordinary pressure at 750° in the presence of alumina was unsuccessful. Therefore, not only temperature and catalyst are necessary for the isomerization of the relatively stable cycloparaffins but also pressure. With the 3-membered ring, the product was an olefin; but in the case of the 6-membered system the change was into the more stable (according to Baeyer's hypothesis) 5-membered ring. However, it must be realized that the absence of hexene in the lower boiling fraction of the product is not conclusive evidence that hexene was not formed, either primarily from cyclohexane or subsequently through methylcyclopentane.

I have made recent experiments on the hydrogenation of various aromatic compounds at high temperatures (about 450°) and high pressures (see " Destructive Hydrogenation") which show that the isomerization of 6-membered rings into 5-membered rings is a common occurrence in the presence of catalysts. For example, the hydrogenation of phenol, in the presence of mixed nickel oxide—aluminum oxide catalyst at 450° and under an initial hydrogen pressure of 100 atmospheres produces up to 90% yield (by weight) of a mixture of cyclohexane and methylcyclopentane.

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[1] Kischner, J. Russ. Phys. Chem. Soc., *29*, 594 (1897).

Isomerization of 4-Membered Rings

At that time the proof of the structure of the hydrocarbon obtained by Gustavson and called by him vinyltrimethylene represented a difficult problem since very little was known about saturated cyclic hydrocarbons containing an unsaturated side chain. The first investigations on this hydrocarbon were carried out in collaboration with Tikhotzky.[1] For the preparation of vinyltrimethylene Gustavson's directions were slightly modified. The action of nitrosylchloride resulted in the formation of a crystalline nitrosylchloride addition product, melting at 78°, which showed analytical values corresponding to the formula C_5H_8NOCl. The yield, however, was small.

When 10 g. of vinyltrimethylene (b.p., 42°) was passed, during 80 minutes, through a glass tube containing alumina at 300° an isomeric transformation took place as shown by the following evidence. The main product (there was also a small low boiling and a small high boiling fraction) boiled at 39° and did not form a solid addition product with nitrosylchloride. With bromine it formed a liquid bromide which contained less than two molecules of bromine per molecule of hydrocarbon. Six grams of the hydrocarbon was treated with an acetic acid solution of hydrogen bromide. The product was separated by distillation into two fractions, 3 g. boiling at 70–74° and 3.5 g. at 110–111°. The first fraction, according to its density (1.2) and its analysis, was the product resulting from the addition of one molecule of hydrogen bromide to the hydrocarbon C_5H_8, namely, C_5H_9Br. This bromide did not decolorize permanganate solution and, therefore, must have possessed a ring structure but not a double bond. The second fraction, according to its density (1.7) and analysis, resulted from the addition of two molecules of hydrogen bromide to C_5H_8 to form $C_5H_{10}Br_2$ which fact is evidence for the opening of the ring of vinyltrimethylene under the influence of alumina and for the formation of two double bonds, and there is some reason to believe that the hydrocarbon product was an allene. However, the reactions of this dibromide must be studied in order to throw more light upon the structure of its parent hydrocarbon.

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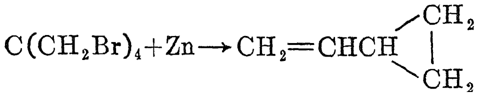
[1] Ipatieff and Tikhotzky, J. Russ. Phys. Chem. Soc., *36*, 760 (1904).

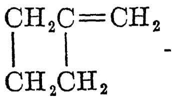
On the other hand, the simultaneous formation of the saturated monobromide suggested the possibility that the supposed vinyltrimethylene was really a mixture of two isomers. Further investigation on the structure of this interesting hydrocarbon and upon its catalytic rearrangement was made, at my suggestion, by one of my graduated students, Filipov.[1]

Gustavson obtained the product, to which he erroneously ascribed the structure of vinyltrimethylene, by the action of zinc dust upon an alcoholic solution of pentaerythritol tetrabromide, on the assumption of the following reaction:

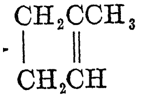


Filipov was able to separate the product, by means of repeated fractionation, into two isomers. Hydrogenation under pressure and at ordinary temperature in Ipatieff's bomb in the presence of either platinum or nickel gave the same product (boiling at a constant temperature), whether starting from the separate isomers or from the mixture. All evidence pointed to the conclusion that Gustavson's vinyltrimethylene must have been a 4-membered ring and that the two isomers were methylenecyclobutane (I) and methylcyclobutene (II).

In the presence of alumina at 300°, methylenecyclobutane undergoes rearrangement into methylcyclobutene.



(I)



(II)

In recent years the Badische Anilin Fabrik and also Dojarenko[2] have studied the isomeric transformations of hydrocarbons and alcohols under the influence of alumina and have been especially interested in the preparation of isoprene (of interest with regard to synthetic rubber) by the rearrangement of various hydrocarbons possessing the empirical formula C_5H_8. As early as 1912 there was a patent covering the isomerization of dimethylallene into isoprene under diminished pressure in the presence of alumina.

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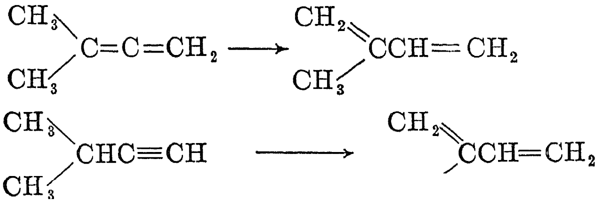
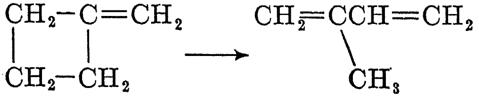
[1] Filipov, J. prakt. Chem., *93*, 162–182 (1916).

[2] Dojarenko, J. Russ. Phys. Chem. Soc., *58*, 1 (1926).

When in 1896, I had occasion to prepare a large quantity of dimethylallene in the laboratory of Adolf von Baeyer in Munich for the purpose of synthesizing isoprene, I observed that the higher the concentration of the alkali solution employed in the reaction, the higher the boiling point of the hydrocarbon product (boiling point of dimethylallene, 40°; of isoprene, 32–33°). At that time, it was assumed that the isomerization of dimethylallene into isoprene was taking place and that this transformation was catalyzed by alkali and by pressure. I communicated my observations to A. Favorsky, the first investigator of the isomeric transformations of the C_nH_{2n-2} series of hydrocarbons, and his subsequent studies and the patents of the Badische Anilin Fabrik have fully confirmed my supposition. Another patent, taken out by the same concern, indicated that isopropylacetylene is converted into isoprene under the influence of alumina, the operating conditions being 50 mm. pressure and 400° temperature.



Dojarenko[1] worked with an especially purified methylenecyclobutane and obtained transformation into isoprene at 400–430° in the presence of alumina.



He also observed other reactions—polymerization, dehydration, etc.,—the polymerization product being a rubbery material. He was also able to transform methylcyclopropane into isobutylene at 340–360° which corresponds to the rearrangement observed earlier by myself, of dimethylcyclopropane into trimethylethylene.

Dojarenko also studied the transformations of the cyclic alcohols of formula C_4H_8O, using similar experimental conditions. Preliminary dehydration of the alcohol was followed by rearrangement of the resulting hydrocarbon. Under these conditions, the first formed hydrocarbons (C_nH_{2n-2}) decomposed into olefins with separation of carbon. The chief product was propylene since the intermediate butadiene was not stable under the conditions of the experiment.

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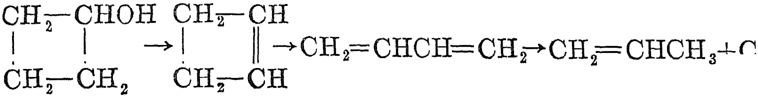
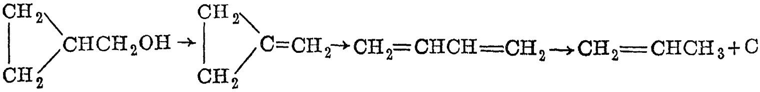
[1] Dojarenko, J. Russ. Phys. Chem. Soc., *58*, 1 (1926).

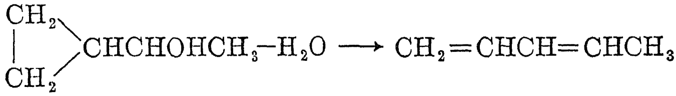


Cyclopropyl carbinol was found to behave in the same manner.



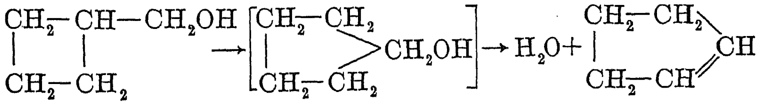
These are interesting examples of the transformation of 3- and 4-membered rings into open chain olefins. The tendency of 3-membered rings to go over into the more stable 4-membered system is evident. Dojarenko also investigated the behavior of cyclic alcohols of formula $C_5H_{10}O$ under similar conditions, studying methylcyclopropyl carbinol, methylcyclobutanol, and cyclobutyl carbinol.

Methylcyclopropyl carbinol dehydrates and the ring opens, the main product being methylbutadiene (piperylene).



It is very probable that the first step is the isomerization of a 3-membered into a 4-membered ring and that it is the latter that loses water to form the diolefin.

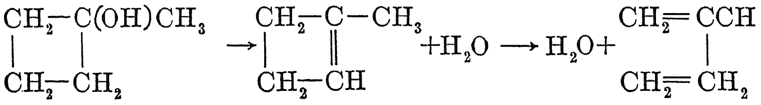
Alumina is able to promote the transformation of 4-membered into 5-membered rings. Thus, from *cyclobutyl carbinol* at 415–430° was obtained a good yield of cyclopentene (III). It is possible that water was eliminated, not from the starting material, cyclobutanol (I), but from the intermediately formed cyclopentanol (II).



(I) (II) (III)

Under the conditions of the experiment, cyclopentene is sufficiently stable to resist rearrangement into an open chain compound (presumably, isoprene) and, therefore, there are no polymerization products.

On the other hand, methylcyclobutanol, which has a nuclear hydroxyl group, behaves in a totally different manner in the presence of alumina.



The intermediate methylcyclobutene rearranges and the chief product of the reaction is isoprene.

These experiments with various cyclic compounds confirmed our opinion of the relatively greater stability of the open chain olefins and also indicated the importance of the structure of these cyclic compounds upon the course of the reaction.

Metameric Catalytic Transformation

Catalytic transformations in which the chemical function of the material is not changed are called isomerizations, and, likewise transformations which take place with change in chemical function might be called metameric isomerization.

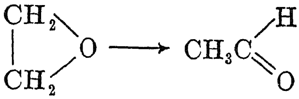
Together with Leontovitch,[1] experiments were made on the decomposition of alpha-oxides. These substances, when passed through a glass tube, begin to decompose only at 500°, suffering partial conversion into aldehydes and ketones. However, when organic acids are passed through a tube containing alumina, decomposition commences at 200–300° with the formation of aldehydes and ketones *metameric* with alpha-oxides. The alpha-oxides were prepared from glycol chlorohydrins which, in turn, were obtained by the addition of hypochlorous acid to olefins, and the latter were prepared by the catalytic dehydration of alcohols in the presence of alumina.

The oxides were carefully heated in a small flask and the vapors were passed through a small glass tube containing alumina, the tube being heated in the usual furnace.

Ethylene oxide was obtained from the chlorohydrin of monoacetylglycol by heating with potassium hydroxide. Ten grams of

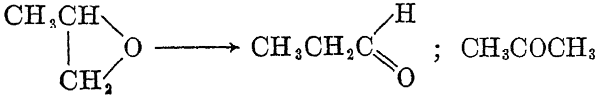
[1] Ipatieff and Leontovitch, Ber., *36*, 2016 (1903).

the oxide was passed over alumina at 200° during 15 minutes. The 6 g. of liquid which collected in the receiver boiled at 20–30° and instantaneously reduced an ammoniacal solution of silver oxide. When the product was diluted with an equal volume of ether, and ammonia was passed into the solution, a crystalline mass was obtained, which was the aldehyde addition product, melting point 76–78°. Thus, ethylene oxide undergoes catalytic metameric transformation into acetaldehyde in the presence of alumina.



Propylene oxide (11 g.), boiling point 34–35°, was passed over ignited alumina at 250–260° during two hours. The liquid condensate (9 g.) boiled chiefly at 50–75°; a small amount boiled up to 140°. There was very little secondary product. The fraction boiling at 50–75° produced a mirror with Tollen's reagent and the iodoform test showed the presence of a very small amount of acetone. It was refluxed several hours with aqueous silver oxide, and after standing for one day, the small quantity of acetone present was removed by steam distillation. The solution was filtered from silver oxide and crystallized. The resulting silver salt (about 4 g.) was found to be silver propionate, analyzing for 59.9% of silver whereas the theoretical for $C_3H_5O_2Ag$ is 59.6%.

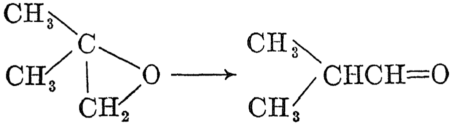
Therefore, propylene oxide is metamerically converted into propionaldehyde by the catalytic action of alumina, with simultaneous formation of a very small amount of acetone.



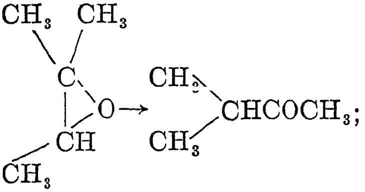
Isobutylene oxide, boiling point 50–51.5°, was the starting material. In one experiment, 18 g. of the oxide was passed through a large glass tube containing alumina, the tube being heated to 400° in a gas furnace. In another experiment the oxide was passed through a small tube containing alumina at 310°. The results were the same in both cases; the liquid product boiled at 61–70°. When this liquid was treated with sodium bisulphite solution, a solid was obtained, which on decomposition with sodium carbonate solution regenerated isobutyraldehyde, which yielded silver isobutyrate with freshly precipitated silver oxide.

Anal. Calcd. for $C_4H_7O_2Ag$: Ag, 55.4%. Found: Ag, 55.4%.

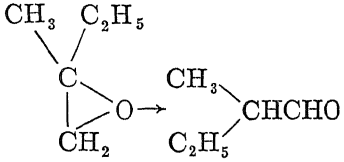
Consequently, it is evident that isobutylene oxide undergoes metameric transformation into isobutyraldehyde, under the influence of alumina.



Trimethylethylene oxide (boiling point, 73–76°) containing a small amount of unsym-methylethylethylene oxide, was passed over alumina at 250–260°, 10 g. during 150 minutes. The liquid product (8.5 g.) boiled at 73–90°. From the product was separated a fraction (boiling point, 90–98°) which, on standing with sodium bisulphite solution, gave a crystalline product; this fraction also reduced ammoniacal silver oxide solution. Evidence was obtained to justify the conclusion that trimethylethylene oxide (I) is metamerized into methylisopropyl ketone (II) and unsym-methylethylethylene oxide (III) into unsym-methylethylacetaldehyde (IV).

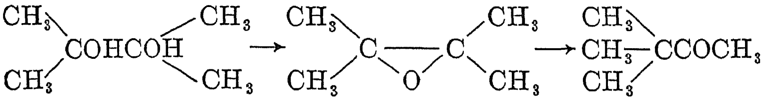


(I) (II)



(III) (IV)

Pinacone (V) is converted at 300–320°, in the presence of alumina, first into the corresponding oxide (VI) and then into the ketone, pinacolone (VII).



(V) (VI) (VII)

A number of experiments were made on the decomposition of amylene oxide in the absence of alumina. Transformation into carbonyl compounds does not take place at 300°, but starts only at 500°. At 600° the decomposition of amylene oxide proceeds rapidly, but there is also considerable decomposition of the carbonyl product, with liberation of gas.

For example, 23 g. of amylene oxide was passed through an empty glass tube during 135 minutes at 500°. There was very little gas formation. The boiling point of the condensate was 86–98° and Tollen's reagent showed the presence of a small amount of aldehyde. Crystals were slowly deposited when the liquid was contacted with aqueous sodium bisulphite for one day. The conclusion is that the transformation of amylene oxide into aldehyde and ketone started at 500°.

In another experiment, 22 g. of amylene oxide was passed through an empty glass tube at 600° for 50 minutes. Six liters of gas was obtained, which has the following composition: C_nH_{2n}, 32.3%; CO_2, 0.6%; CO, 29.6%; C_nH_{2n+2} and H_2, 37.5%. Ten grams of liquid was also produced. Tests indicated the presence in the latter of methylisopropyl ketone and methylethylacetaldehyde. A silver salt was obtained by treating 3 g. of the liquid product with moist silver oxide.

Anal. Calcd. for $C_5H_{10}OAg$; Ag, 51.7%. Found: Ag, 51.8%.

That the metameric transformation of alpha-oxides into aldehydes and ketones is promoted by zinc chloride was already known, having been first observed by Kashirsky [1] and later investigated in a thorough manner by Krasussky [2] who showed that lead chloride is also a catalyst for this reaction. Thus, these two chlorides play a rôle similar to alumina in the decomposition of alpha-oxides.

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[1] Kashirsky, J. Russ. Phys. Chem. Soc., *13*, 76 (1881).

[2] Krasussky, *ibid.*, *34*, 543 (1902).

CHAPTER V

HYDROGENATION

As already mentioned, I was studying the dehydrogenation of alcohols under the influence of catalysts at the same time that Sabatier and Senderens were studying the catalytic hydrogenation of organic compounds. This circumstance, of course, was suggestive of the fact that we were dealing with a reversible catalytic process of hydrogenation and dehydrogenation, but there was another reason which induced me from the beginning of my investigations (i.e., since 1901) to test the reversibility of catalytic reactions by means of experiment. First of all, iron and zinc in their usual state were, as my investigations have shown, catalysts in the dehydrogenation of alcohols, and no one had studied their application for the reaction of hydrogenation; on the other hand, nickel, both in its usual state and also in finely dispersed form cannot catalyze the hydrogenation of aldehydes at ordinary pressure because it vigorously decomposes them into carbon monoxide and saturated hydrocarbons.

Thus, in 1904, immediately after finishing my experiments on the dehydrogenation and dehydration of alcohols under high pressures, I started the study of the hydrogenation of organic compounds in a newly designed high pressure apparatus. These experimental results were sent in November, 1905, to the editorial office of the Journal of the Russian Physical Chemistry Society and were published in the first issue of the Journal in 1906.[1] This represented the first work on the hydrogenation of organic compounds in the presence of molecular hydrogen under pressure in the liquid phase [2] and it clearly showed that it was not true that catalysis proceeds only when the vapors of the organic material come into contact with the catalyst as stated by Sabatier and Senderens.

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[1] Ipatieff, J. Russ. Phys. Chem. Soc., *38*, 75 (1906); C.A., *1*, 1538 (1907).

[2] I take the present occasion to make the following remark. Stanley G. Greene, in his book "Industrial Catalysis," page 226, indicates that Fokin was the first to hydrogenate in the liquid phase under pressure with the catalyst suspended in the liquid being hydrogenated and that Ipatieff's contribution was to generalize and systemize this previous work of Fokin. That this is not true may be easily verified by the dates of these respective investigations. My first results on the liquid phase hydrogenation under pressure were obtained in 1904–1905 and published in the first issue of the Journal of the Russian Physical Chemical Society for 1906 whereas the article by Fokin appeared two years later, J. Russ. Phys. Chem. Soc., *39*, 607 (1907); *40*, 276 (1908).

In order to decide the question of the reversibility of the catalytic decomposition of alcohols into aldehydes, ketones, and hydrogen, it was necessary to carry out this reaction in a closed system in the presence of a suitable catalyst. Of course, this problem could be approached from the opposite direction, namely, by allowing aldehydes and ketones to react in a closed vessel with hydrogen in the presence of various catalysts. In order to study this hydrogenation reaction it was necessary to have an apparatus capable of operating under high pressure and at elevated temperature and also a pump for the introduction of hydrogen. This phase of study was started as soon as the necessary equipment was assembled.

Considerable experimental difficulty was foreseen, since aldehydes are relatively reactive substances, liable to undergo secondary decomposition and also condensation reactions. Moreover, high temperature was necessary since iron does not catalyze aldehyde reduction at low temperatures.

$$C_nH_{2n+1}OH \rightleftarrows C_nH_{2n}O + H_2$$

Experiments made at ordinary pressure in which the reactants were passed over various catalysts were not significant since it is difficult to make certain that true equilibrium had been attained.

The experiments about to be described are not sufficient to answer many questions on this problem, but they do throw light upon certain aspects of it, and offer methods for the catalytic preparation of various substances impossible to obtain at ordinary pressure.

My first experiments were made on the reduction of aldehydes to alcohols in the presence of an iron catalyst at a temperature not above 450°. For this purpose, a certain amount of acetaldehyde was placed in the apparatus, hydrogen was pumped in to a pressure of 60 atmospheres, and the apparatus was maintained at the desired temperature for a definite length of time. The pressure remained constant and analysis of the gas indicated only decomposition of aldehyde into carbon monoxide and methane and the formation of condensation products.

Since acetone is a much more stable compound, I next studied its reduction by hydrogen in the presence of an iron catalyst.

Two experiments were made, Nos. 512 and 513, in which 40 g. of acetone was placed in the iron high pressure apparatus, hydrogen being pumped in to 101 atmospheres, and the temperature maintained at 400°. The curve picturing the course of the reaction (Fig. 18) indicates that as the reduction proceeded, the pressure in the apparatus dropped for 16 hours, and finally became constant.

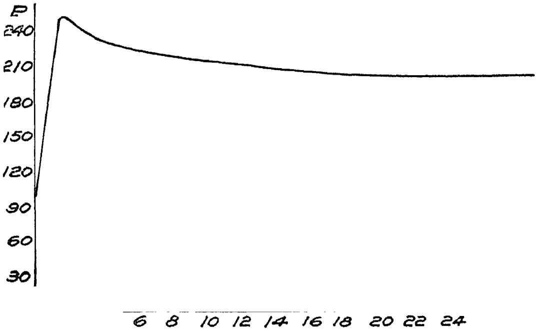

FIG. 18

In each of the above experiments, the pressure in the apparatus after cooling was found to be 59 atmospheres. The gas collected in the gasometer was analyzed; its composition was as follows:

CO, 0.0%; C_nH_n, 0.2%; CO_2, 1.8%; H_2, 80.2%; C_nH_{2n+2}, 16.2%

The liquid product, 36 g., was shaken with water, and the upper layer (about 11 g.) which was insoluble in water, was separated by means of a pipette, dried with calcium chloride, and distilled. The liquid boiled at 60–180°, decolorized permanganate solution, and added bromine with the evolution of hydrogen bromide. This liquid has not yet been investigated, but, according to all probabilities, is a mixture of C_nH_{2n} hydrocarbons.

The water extract of the liquid product was saturated with potash, and the upper layer was dried with potash and distilled. The liquid distilled at 60–85° and, according to its properties, represents a mixture of acetone and isopropyl alcohol. The higher boiling fraction, b.p., 80–84°, did not combine with bisulphite, mixed with water in all proportions, evolved hydrogen by the action of sodium, and reacted vigorously with phosphorus pentachloride with the liberation of hydrogen chloride.

Available data indicate that iron is a catalyst for both the decomposition of alcohols into ketones and for the reduction of ketones into alcohols; in other words, we are dealing with a reversible reaction.

$$CH_3CH(OH)CH_3 \rightleftharpoons H_2 + CH_3COCH_3$$

There are experimental difficulties due to side reactions. In the presence of iron, the alcohol may be hydrogenated further to a hydrocarbon which will decompose into methane and olefin and the latter may polymerize into hydrocarbons of formula C_nH_{2n} (as shown in a preceding chapter). Whether or not it will be possible to convert aldehydes into alcohols in the presence of iron, depends upon whether this reaction takes place more readily than does the decomposition of the aldehydes.

Ipatieff and Balatchinsky [1] investigated the reversibility of the hydrogenation of acetone in the presence of copper oxide and zinc dust, these experiments being performed in the high pressure apparatus in an iron tube. In order to study the catalytic action of copper oxide and zinc dust, a tube of phosphor bronze would have been suitable except that copper walls have a bad effect upon hydrogenation. For that reason, an iron tube was employed. But iron is also an hydrogenation catalyst for ketones and aldehydes, and in order to determine the quantitative effect of iron at 280–300° a blank experiment was run. Acetone was placed in the iron apparatus, hydrogen was pumped in, and the apparatus was heated for 30 hours at 300°. Investigation of the product showed that the acetone did not suffer any change under these conditions; there was a very small amount of condensation products.

Copper Oxide.—Forty grams of acetone and 3 g. of copper oxide were placed in the high pressure apparatus, and a hydrogen pressure of 100–120 atmospheres was imposed. The apparatus was heated for 30 hours at 280–300° until the pressure no longer diminished. The product distilled, for the most part, at 80–83°, and was identified as isopropyl alcohol, the yield being about 65%. A small amount of acetone was always present, even after long heating. Besides these two substances, there were also unsaturated condensation products. Thus, the hydrogenation of acetone in the presence of copper oxide is reversible.

Zinc Dust.—Forty grams of acetone and 5 g. of zinc dust were placed into the high pressure apparatus together with a hydrogen pressure of 130 atmospheres. The apparatus was heated at 200–

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[1] **Ipatieff and Balatchinsky, Ber., *44*, 3459 (1911).**

300° for 23 hours. A considerable lowering of the pressure indicated that hydrogenation was taking place. Distillation showed the product to consist mainly of isopropyl alcohol (b.p., 80–83°); yield about 50%.

To determine the amount of residual acetone, the lower boiling fraction was treated with sodium bisulphite. It was found that about 25% of the original acetone still remained. There was greater formation of condensation products with zinc dust than with copper oxide.

To show that zinc dust is also a catalyst for the opposing reaction, dehydrogenation, isopropyl alcohol, and zinc dust were placed in the high pressure apparatus and hydrogen was added until a pressure of 40 atmospheres was reached, i.e., the same amount of hydrogen which remained after the hydrogenation of acetone in the preceding experiment. The apparatus was heated to 300°. Increase in pressure during the experiment indicated that dehydrogenation of isopropyl alcohol was taking place and the investigation of the reaction product established without doubt the formation of acetone. Thus, in the presence of these catalysts the reaction is reversible.

Next, I turned my attention to another catalyst, reduced nickel, because Sabatier and Senderens [1] had shown in a series of experiments that nickel, reduced by hydrogen, is able to catalyze the reduction of aldehydes and ketones, and unsaturated hydrocarbons as well, at relatively low temperatures. Sabatier and Senderens had also shown that reduced nickel can promote the catalytic decomposition of alcohols into aldehydes, ketones, and hydrogen similar to that which I had previously [2] observed in the case of iron, zinc, and highly dispersed metals, such as tin, copper, etc., reduced from the oxides.[3]

But reduced nickel is distinguished from iron and zinc by the fact that the aldehydes or ketones obtained from the alcohol, even at low temperatures (178°), decompose further into carbon monoxide and saturated hydrocarbons (Sabatier and Senderens). Therefore, reduced nickel cannot be considered as a suitable catalyst for the preparation of aldehydes and ketones from alcohols. For this purpose I had shown [2] that iron and zinc (not reduced by hydrogen) were quite suitable.

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[1] Sabatier and Senderens, Compt. rend., *136*, 982 (1903).

[2] Ipatieff, Ber., *34*, 596 (1901).

[3] Ipatieff, Ber., *35*, 1047 (1902); *35*, 1057 (1902).

However, since Sabatier had observed that reduced nickel was able to catalyze both reactions (at ordinary pressure), dehydrogenation of alcohols and hydrogenation of aldehydes and ketones, it was of interest to investigate the action of this catalyst under superatmospheric pressure. The experiments about to be reported are only my first ones; I am still continuing this work.

A certain amount of aldehyde or ketone and 3–4 g. of reduced nickel were placed in the high pressure apparatus. The reduced nickel was obtained by the dry hydrogen reduction of the oxide, the latter being furnished by Kahlbaum (Berlin). Hydrogen was pumped into the tube and the apparatus was heated to a definite temperature. Time and pressure were recorded and the reaction was considered to be at an end when the pressure no longer diminished.

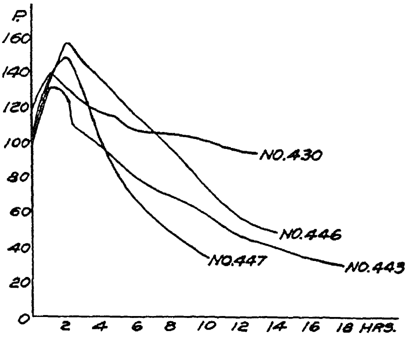

FIG. 19

It is evident that my experimental conditions differed greatly from those of Sabatier and Senderens. These investigators considered it of great importance that the catalyst should not be wetted with liquid; in my experiments the nickel was in the liquid. Sabatier and Senderens were very careful about the purity of the reduced nickel; I paid no attention to its purity.

Hydrogenation experiments were made with the following substances: acetone, methylethyl ketone, benzaldehyde, and camphor.

Should there be insufficient hydrogen for complete hydrogenation, the tube could be cooled and more hydrogen be added, after which the tube could be heated again.

The data are collected in Table 38 (see Fig. 19).

The following conclusions may be drawn.

(1) The hydrogenation of ketones under high pressure in the presence of nickel and excess hydrogen proceeds to completion as shown by the absence of ketone in the product.

(2) Hydrogenation under high pressure proceeds rather slowly as seen from the curves of the pressure change.

TABLE 38

REDUCTION OF KETONES IN THE PRESENCE OF NICKEL CATALYST

EXPT. No.	SUBSTANCE AND AMOUNT	INITIAL HYDROGEN PRESSURE, 1ST TIME, ATMS.	FINAL PRESSURE, 1ST TIME, ATMS.	INITIAL HYDROGEN PRESSURE, 2ND TIME, ATMS.	FINAL PRESSURE, 2ND TIME, ATMS.	TIME OF HEATING, HRS.	T., °C.	$(dp/dt)_{max}$ K.M.	LIQUID PRODUCTS	GAS PRODUCTS
443	Acetone, 40 g.	100	29			16	198	0.6	Pure isopropyl alcohol	Hydrogen
446	Methylethyl Ketone, 72 g.	119	28	120	45	26	195	0.4	Pure methylethyl carbinol	Hydrogen
447	Methylethyl Ketone, 72 g.	121	20	121	48	29	198	0.45	Pure methylethyl carbinol	Hydrogen
430	Benzaldehyde	101	50			15	198	0.4	Toluene and methylcyclohexane	Hydrogen
482	Camphor, 35 g.	129	102			18	200		Borneol	Hydrogen

(3) No decomposition of the reduction products or of their condensation products takes place although heating at 200° was continued for a long time at high pressure.

(4) Aromatic aldehydes are not reduced to alcohols, but still further, into aromatic and hydroaromatic hydrocarbons. Hydrogenation proceeds in spite of the presence of water.

(5) Alcohols are obtained under these conditions in theoretical yield and require after distillation no further purification. High pressure catalytic hydrogenation furnishes a very convenient method for the preparation of secondary alcohols.

In exactly the same way camphor was hydrogenated into borneol in the presence of nickel, but it was difficult to follow the pressure drop because the camphor sublimed and plugged the manometer. Nevertheless, it is an excellent preparative method for borneol, the product melting at 210°.

The next subject to be studied was the behavior of aliphatic alcohols and ethers (40 g. in each experiment) under the influence of reduced nickel, with and without hydrogen. The data from these experiments are summarized in the following table.

After comparing the products of decomposition with those obtained in the presence of an iron catalyst, we come to the following conclusions.

(1) At 195° and under high pressure of hydrogen, ethyl alcohol does not decompose; decomposition starts only when the temperature reaches 300° and proceeds slowly (Expt. 424), the pressure remaining constant during the last two hours. The decomposition products are acetaldehyde and saturated hydrocarbons. When alcohol is heated in the absence of hydrogen pressure at 210° (Expt. 425), the same reaction occurs, with the difference that carbon monoxide is among the reaction products, this substance being absent in the presence of hydrogen.

(2) The decomposition of alcohols in the presence of reduced nickel does not yield olefin hydrocarbons, neither in the presence or the absence of hydrogen. This circumstance is explained by the observation of Sabatier and Senderens that nickel promotes the conversion of ethylene into ethane, even at low temperature. Iron and zinc do not possess this ability in such a high degree and, therefore, when alcohol is decomposed in the presence of iron and zinc at high pressure, there is always a small amount of olefin present. In the case of catalysis by nickel it is very probable that ethyl-

TABLE 39

High Pressure Reduction of Alcohols and Ether in the Presence of Hydrogen and Reduced Nickel

Expt. No.	Alcohol	Initial Pressure of Hydrogen, Atms.	T., °C.	Maximum Press., Atms.	Time, Min.	Analysis of Gas in %				Final Press. after Cooling, Atms.	Gaseous Products, Liters	Liquid Products, Grams
						CO_2	CO	H_2	C_nH_{2n+2}			
422	Ethyl Alcohol	89	195	131	540			92		86		
424	Ethyl Alcohol	82	290	220	540	5.0		59	36	98	26.8	
425	Ethyl Alcohol		290	110	480	12.4	8.0	31.2	47.8	48	11.7	20
445	Methyl Ether	88	200–300	126	1215			80.8	19.0	32	8	32
446	Methyl Alcohol	100	320	320	780		2.6	71.6	25.8	130	20	25

ene hydrocarbons are formed in the first phase, but are immediately hydrogenated into saturated hydrocarbons. Likewise, in the decomposition of *methyl ether* only saturated hydrocarbons are formed. The reaction proceeds very slowly at 300° and the temperature must be increased if complete decomposition of the ether is desired.

(3) Experiments indicate that in the reduction of aldehydes by hydrogen in a closed vessel in the presence of a nickel catalyst the temperature cannot be increased up to 290° because of the decomposition of aldehyde and alcohol which takes place in spite of the excess of hydrogen. An exact determination of the temperature limits within which the reduction of aldehydes and ketones proceeds with the greatest velocity without decomposition, as well as the study of the conditions of equilibrium is being made at the present time.

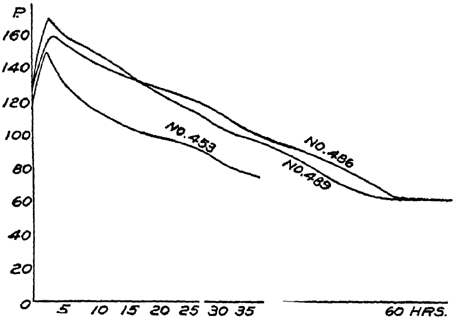

FIG. 20

An investigation is also being made of a number of substances which cannot be hydrogenated by the method of Sabatier and Senderens because of their high boiling points. According to the method of these French chemists, the substance must be passed over the nickel catalyst in the vapor state and many substances would decompose under these conditions. These data are presented in Table 40 and the pressure curves showing the course of the reaction in Fig. 20.

Blank runs (Expts. 485-a and 485-b) were made in order to determine the pressure change of hydrogen with temperature, with and without reduced nickel; the nickel was found to have no effect.

The following conclusions are based on the data presented in the preceding tables and also Table 40.

(1) Hydrogenation of the benzene nucleus, under the influence

TABLE 40

Expt. No.	Substance and Amount	Catalyst	Initial Hydrogen Pressure, 1st Time, Atms.	Final Pressure, 1st Time, Atms.	Initial Pressure, 2nd Time, Atms.	Final Pressure, 2nd Time, Atms.	Initial Pressure, 3rd Time, Atms.	Final Pressure, 3rd Time, Atms.	Time, Hours	T., °C.	$(dp/dt)_{max}$ K.M.	Analysis of Gas	Reaction Products
463	Phenol, 50 g.	Reduced Ni	104	32	110	49	111	48	55.5	238	0.2	Hydrogen	Hexahydrophenol
465	Phenol, 40 g.	Reduced Ni	108	40	102	33			57	215	0.2	Hydrogen	Hexahydrophenol, hexane present
466	Phenol, 35 g.	Reduced Ni	105	50	110	38			58	220	0.2	Hydrogen	The same as in the preceding
467	Phenol, 36 g.	Reduced Ni	125	50	126	76			28.5	240	0.2	Hydrogen	Hexahydrophenol
486	Hydroquinone, 30 g.	Reduced Ni	128	39					63	215	0.07	Hydrogen	Quinite
489	Hydroquinone, 30 g.	Reduced Ni	120	38					64.5	215	0.09	Hydrogen	Quinite
453	Benzoin, 30 g.	Reduced Ni	110	50					35	200	0.1	Hydrogen	Dibenzyl
406	Benzene, 40 g.	Fe	75	70	Maximum pressure, 224 atms.				3.3	500		Hydrogen	Benzene

of high pressure (up to 220 atmospheres) and high temperature, does not proceed in the presence of reduced copper, powdered aluminum (Expts. 418 and 426), or of iron (Expt. 406).

(2) Hydrogenation of the benzene ring takes place in the presence of nickel in a closed vessel under high pressure. This reaction goes to completion but the speed of reaction is slow without stirring; that is, the value $(dp/dt)_{\max}$ is small. Hydrogenation is especially slow in the case of mono- and dihydric phenols.

(3) Benzyl alcohol, similar to benzaldehyde, is reduced to toluene by hydrogen under pressure in the presence of nickel, some of the toluene hydrogenating further to hexahydrotoluene. The same result was obtained by Gdanovitch [1] in the catalytic hydrogenation of benzyl alcohol in the presence of aluminum at ordinary pressure; in this case, the final product was the aromatic hydrocarbon, toluene. Darzens [2] observed the same reaction using catalytic nickel.

(4) It was interesting to find out whether a carbonyl group in an aliphatic chain would be reduced. For this purpose benzoin was subjected (Expt. 453) to a temperature of 200° in the presence of hydrogen and catalytic nickel until the pressure in the apparatus became constant. The contents of the tube were extracted with ether and the product of the reaction was crystallized from alcohol. The material was identified as dibenzyl, melting point 51°.

Anal. Calcd. for $C_{14}H_{16}$: C, 91.2%; H, 8.6%. Found: C, 90.3%, 90.7%; H, 7.5%, 7.9%.

Thus, complete reduction of both the carbonyl and the hydroxyl groups had occurred:

$$C_6H_5COCHOHC_6H_5 + 3H_2 \rightarrow C_6H_5CH_2CH_2C_6H_5 + 2H_2O$$

Therefore, it might be concluded that in the presence of reduced nickel, the oxygen present in the side chain of aromatic compounds in the form of carbonyl and hydroxyl groups is completely substituted by hydrogen.

(5) Benzene is hydrogenated quantitatively (Expts. 471, 472) to cyclohexane of a high degree of purity. Nitration mixture does not act at all upon the cyclohexane prepared under high hydrogen pressure; it distills within one degree without residue and in snow solidifies to a white crystalline mass. By this method it is very easy

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[1] Gdanovitch, J. Russ. Phys. Chem. Soc., *36*, 765 (1904).

[2] Darzens, Compt. rend., *139*, 868 (1904).

TABLE 40

Expt. No.	Substance and Amount	Catalyst	Initial Hydrogen Pressure, 1st Time, Atms.	Final Pressure, 1st Time, Atms.	Initial Pressure, 2nd Time, Atms.	Final Pressure, 2nd Time, Atms.	Initial Pressure, 3rd Time, Atms.	Final-Pressure, 3rd Time, Atms.	Time, Hours	T., ° C.	$(dp/dt)_{max}$ K.M.	Analysis of Gas	Reaction Products
463	Phenol, 50 g.	Reduced Ni	104	32	110	49	111	48	55.5	238	0.2	Hydrogen	Hexahydrophenol
465	Phenol, 40 g.	Reduced Ni	108	40	102	33			57	215	0.2	Hydrogen	Hexahydrophenol, hexane present
466	Phenol, 35 g.	Reduced Ni	105	50	110	38			58	220	0.2	Hydrogen	The same as in the preceding
467	Phenol, 36 g.	Reduced Ni	125	50	126	76			28.5	240	0.2	Hydrogen	Hexahydrophenol
486	Hydroquinone, 30 g.	Reduced Ni	128	39					63	215	0.07	Hydrogen	Quinite
489	Hydroquinone, 30 g.	Reduced Ni	120	38					64.5	215	0.09	Hydrogen	Quinite
453	Benzoin, 30 g.	Reduced Ni	110	50					35	200	0.1	Hydrogen	Dibenzyl
406	Benzene, 40 g.	Fe	75	70	Maximum pressure, 224 atms.				3.3	500		Hydrogen	Benzene

of high pressure (up to 220 atmospheres) and high temperature, does not proceed in the presence of reduced copper, powdered aluminum (Expts. 418 and 426), or of iron (Expt. 406).

(2) Hydrogenation of the benzene ring takes place in the presence of nickel in a closed vessel under high pressure. This reaction goes to completion but the speed of reaction is slow without stirring; that is, the value $(dp/dt)_{\max}$ is small. Hydrogenation is especially slow in the case of mono- and dihydric phenols.

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Thus, complete reduction of both the carbonyl and the hydroxyl groups had occurred:

$$C_6H_5COCHOHC_6H_5 + 3H_2 \rightarrow C_6H_5CH_2CH_2C_6H_5 + 2H_2O$$

Therefore, it might be concluded that in the presence of reduced nickel, the oxygen present in the side chain of aromatic compounds in the form of carbonyl and hydroxyl groups is completely substituted by hydrogen.

(5) Benzene is hydrogenated quantitatively (Expts. 471, 472) to cyclohexane of a high degree of purity. Nitration mixture does not act at all upon the cyclohexane prepared under high hydrogen pressure; it distills within one degree without residue and in snow solidifies to a white crystalline mass. By this method it is very easy

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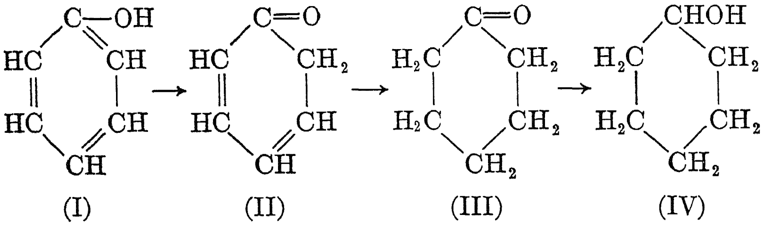
[1] Gdanovitch, J. Russ. Phys. Chem. Soc., *36*, 765 (1904).

[2] Darzens, Compt. rend., *139*, 868 (1904).

to prepare cyclohexane since the apparatus requires no attention once the desired temperature has been reached.

(6) A series of experiments carried out with phenol led to the conclusion that phenols are reduced to cyclohexanol and cyclohexanone; sometimes only cyclohexanol is obtained. At ordinary pressure, as indicated by Sabatier and Senderens, the reduction of phenol with hydrogen in the presence of nickel always yields a mixture of cyclohexanol and cyclohexanone. It is seen that in the experiments in which the temperature reached 235–240° (Expts. 462, 463, 467) a mixture of products was not obtained. On the other hand, in the experiments where the temperature did not exceed 220°, cyclohexanone was always obtained in spite of the fact that hydrogen was in excess at the end of the reaction and that the mixture was heated for a longer time. This formation of ketone from phenol at a low temperature represents an interesting fact which was not observed at all by Sabatier and Senderens.



It is very probable that under the influence of hydrogen, phenol first rearranges from its enolic form (I) to the unstable ketonic form (II), and then adds four atoms of hydrogen at the places where double bonds occur; thus cyclohexanone (III) is obtained as the first product of the reaction, but under the influence of excess hydrogen, it reduces into the alcohol, cyclohexanol (IV). A confirmation of this interpretation is the fact that at a high temperature the ketone is not obtained. Therefore, cyclohexanone cannot be considered to be the decomposition product of cyclohexanol but rather as the primary product of the reaction.

Complete reduction of the ketone into alcohol requires a higher temperature which, of course, increases the velocity of the reduction reaction. Cyclohexanol can be readily prepared by this method and after one distillation it is obtained in a pure state, solidifying in ice to a white crystalline mass.

(7) By the reduction of hydroquinone with hydrogen under high

pressure in the presence of reduced nickel (Expts. 486 and 489), quinite is obtained, the velocity of the reduction being rather low. At the end of the reaction, the product was extracted by alcohol and after removal of the latter (without crystallization), the product melted at 94–97°. It did not reduce Fehling's solution. In order to obtain quinite in a pure state, it was heated with acetic anhydride in ethyl acetate solution. The excess anhydride was removed; the quinite acetate was extracted with ether and finally crystallized. By crystallization it was possible to separate trans-quinite from cis-quinite acetate, the former melting at 102–103°.

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 59.8%; H_2, 8.1%. Found: C, 59.2%, H_2, 7.9%; C, 60.0%, H_2, 7.9%.

Trans-quinite was obtained by saponification of quinite acetate; the melting point was 138–139°.

(8) If the temperature of the high pressure hydrogenation in the presence of reduced nickel exceeds 300° then the result is similar to the hydrogenation at ordinary pressure, namely, the ring splits to form methane as the chief product.

Thus, by heating benzene with hydrogen in the high pressure apparatus at 255° in the presence of reduced nickel (Expt. 559), pure cyclohexane is obtained and, therefore, it is quite possible to obtain cyclohexane at this temperature without fear of decomposition.

TABLE 41

Expt. No.	Substance and Amount	Catalyst	T., ° C.	Initial Press., Atms.	p_{max}, Atms.	Final Press., Atms.	Time, Hrs.	Analysis of Gas in %		Volume of Gas, Liters
								H_2	C_nH_{2n+2}	
559	Benzene, 25 g.	Ni	255	120	184	25	43	H_2		5.1
549	Benzene, 10 g.	Ni	330	112	165	50	5	87.0	12.4	12.0

(9) Above 300°, cyclohexane decomposes in the presence of nickel, partially into benzene, but chiefly into carbon and methane. But, as shown by Expt. 549, a certain equilibrium is reached and within 3 hours the pressure becomes constant. The chief products of the reaction are carbon and cyclohexane.

(10) In order to show that iron is also a catalyst for the conversion of the secondary cyclic alcohols into the ketones and also for the transformation of naphthenes into aromatics, experiments were made with cyclohexane, cyclohexanol (hexahydrophenol), and

with menthol, these substances being heated in an iron tube in the high pressure apparatus.

The results of the experiments are given in Table 42.

Cyclohexane is decomposed at 600–700° in an iron tube into benzene and hydrogen. In order to obtain a large yield of benzene the temperature must not be too high. Thirty-eight grams of cyclohexane (Expt. 460) was passed through an iron tube at 660° during 20 minutes; the product consisted of 19 g. of liquid boiling at 77–81° which on nitration yielded dinitrobenzene, and 9000 cc. of gas having the following composition.

Analysis of Gas: C_nH_{2n}, 12.5; H_2, 70.2; C_nH_{2n+2}, 17.2.

When petroleum was passed through an iron tube, its naphthene content was converted into aromatic hydrocarbons. Cyclohexanol and menthol, in the presence of an iron catalyst, lost two atoms of hydrogen with formation of cyclic ketones. Cyclohexanol was found to decompose readily giving a good yield of cyclohexanone.

When benzene was heated at 600° in the high pressure apparatus in an atmosphere of hydrogen and in the presence of an iron catalyst, diphenyl was formed with liberation of hydrogen (Expts. 547, 548, 554 of Table 42).

$$2C_6H_6 \rightarrow C_6H_5C_6H_5 + H_2$$

In Experiment 554, about 12 g. of crude diphenyl was obtained. The experiment of heating benzene with hydrogen (Expt. 547) at 580° was unsuccessful, due to leakage of hydrogen, either through the seal or through the walls of the tube. These experiments show that the hydrogenation of benzene is not promoted by iron catalysts, even under high temperature and pressure.

HYDROGENATION IN THE PRESENCE OF METALS UNDER PRESSURE [1]

After it was ascertained by preliminary experiments that various organic compounds are hydrogenated under high pressure in the presence of iron, zinc, copper oxide, and nickel, a detailed investigation of this reaction and of its reversibility was undertaken using the high pressure apparatus.

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[1] The first part of the chapter on hydrogenation under high pressure may seem to be rather unsystematically presented. This has resulted from my attempt to present the development of my ideas on catalysis in chronological order and to indicate the exact dates of the most important discoveries in this field. It is to be regretted that the results of my first investigations on high pressure catalytic hydrogenation appeared only in Russian (1905–1906). However, they were abstracted in the Chemisches Centralblatt.

TABLE 42

CATALYTIC DECOMPOSITION OF CYCLOHEXANE, CYCLOHEXANOL, MENTHOL, AND BENZENE UNDER PRESSURE IN THE PRESENCE OF IRON

EXPT. No.	SUBSTANCE	PRESS., ATMS.			TIME, HRS.	T., °C.	FINAL GAS VOL., LITERS	GAS ANALYSIS, % BY VOL.						LIQUID PRODUCT OF REACTION
		Initial of H_2	Max.	Final after Cooling				CO_2	C_nH_{2n}	O_2	CO	H_2	C_nH_{2n+2}	
478	Cyclohexane	0	1 0	143	4.0	600	11.5		2.0	1.0		5.0	92.2	Benzene
479	Cyclohexanol		50	11	4.0	440	3.0		1.8		2.0	82.6	13.4	Cyclohexane
480	Menthol	0	49	14	4.5	450	3.4	8.2	7.6	1.0	16.4	24.6	41.0	Menthene and menthone
547	Benzene, 21 g.	110	297	48	21.0	580	10.7					92.2	7.0	Diphenyl
548	Benzene, 40 g.	0	91	10	4.0	650	0.85					95.2	4.0	Diphenyl
554	Benzene, 40 g.	0	99		5.0	630				Hydrogen				Diphenyl

It should be noted that some scientists, for instance, Paul Sabatier and Stanley Greene, insisted that in my investigations of catalytic reactions I was working only with very high pressures; but there was a necessity of pumping 100 atmospheres of hydrogen into my apparatus at the beginning of the experiments for the sole reason that the capacity of my bomb was small (about 270 cc.). In order that the reaction should proceed to completion, a certain amount of hydrogen was necessary and the "initial pressures" corresponded to this quantity of hydrogen. However, it is easy to see from my work that hydrogenation also takes place at comparatively low pressures. Thus, in Experiments 561 to 565, the initial pressure of hydrogen was only 120 atmospheres and at the end of the reaction after cooling only 11 atmospheres pressure of hydrogen remained, which at 250° would be about 30 atmospheres. [If the hydrogenation of benzene takes place only at very high temperature, I never could have obtained pure cyclohexane; the product would always have contained a certain percentage of benzene.] Furthermore there was a whole series of experiments on the hydrogenation of fats and other compounds carried out with mechanical stirring (see below), in which I could not use high pressures. Hydrogenation was obtained in these experiments and the initial pressures were not above 25–30 atmospheres. In some cases it was necessary to pump hydrogen continuously into the reaction chamber in order to furnish sufficient hydrogen for the reaction.

I consider that Schröter adopted my method *in toto* for the hydrogenation of naphthalene. There are only two differences—first, he used a larger vessel and therefore less hydrogen pressure; second, he worked with a highly purified naphthalene, which is important. The purer the naphthalene, the less hydrogen pressure is required and the faster the reaction. In my first experiments on the hydrogenation of naphthalene, I used the naphthalene as obtained from Kahlbaum whereas Schröter [1] paid serious attention to the purity of his naphthalene and was therefore able to hydrogenate it at a lower pressure.

The same holds true for the criticism by Greene [2] who, discussing the works of Brochet [3] which appeared ten years after my first high pressure investigations, called my conditions of hydrogenation

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[1] Schröter, Ann., *426*, 1 (1922); Wölbing, Hydrierung, Vol. 8, p. 62, Kohle, Koks, Teer, 1926.

[2] S. P. Greene, Industrial Catalysis, p. 279.

[3] Brochet, Compt. rend., *158*, 1351 (1914); Bull. soc. chim., (4), *15*, 554 (1914).

"drastic" and considered the conditions of Brochet who used 15–20 atmospheres as more advantageous. If Brochet succeeded in increasing the velocity of hydrogenation so as to permit the use of lower pressures, this accomplishment must be attributed to the fact that he used more active catalysts obtained through the aid of promoters as shown by my investigations since 1910 with mixed catalysts.

Iron Catalyst

In these experiments, a definite amount of the ketone or aldehyde in question was introduced into the high pressure apparatus and after closing, the necessary amount of dry hydrogen was introduced by means of a pump or directly from a cylinder of the compressed gas. The apparatus was heated in an electric furnace and the course of the reaction was followed by the change in pressure recorded by the pressure gage. Experiments were carried out with acetone, isobutyric and isovaleric aldehydes, and with methylethyl ketone. In Table 43 are presented the results of the experiments on the reduction of acetone by hydrogen in the presence of a catalyst, the whole course of the reaction being shown graphically by the curves.

TABLE 43

Decomposition and Hydrogenation of Acetone and Isopropyl Alcohol under Pressure in the Presence of Iron

Expt. No.	Substance	T., °C.	Press., Atms.			Time, Hrs.	Gaseous Products, Liters	Analysis of Gases, % by Vol.				
			Initial	Max.	Final (Room Temp.)			CO_2	C_nH_{2n}	CO	H	C_nH_{2n+2}
519	Acetone	420	0	102	4	24	1.0	1.6	2.0	37.0	18.8	38.2
521	Acetone	400	0	70	1	24	0.2					
511	Acetone	445	100	248	50	20	14.3	6.0	1.6		16.6	67.0
512	Acetone	400	101	241	59	19	13.2	1.2	0.5	1.8	79.6	16.2
516	Acetone	400	100	270	59	23	14.8	1.4	1.1	3.6	60.8	23.1
518	Acetone	400	103	272	70	20	17.3	0.4		2.8	78.8	14.4
524	(Isopropyl	400	58	187	17	24	2.4	0.8	1.6	8.8	72.0	2.5
515	Alcohol)	400	0	141	18	24	4.0	2.0	4.2	3.0	85.0	4.4

Experiments 519 and 521 were made in order to get an idea of what would happen to acetone when heated alone in an iron tube at 400°, without preliminary introduction of hydrogen. The data are given in Table 43, and the course of the reaction is shown in Curve 521.[1] At this temperature acetone suffered very little change; from 40 g. of acetone about 2–3 cc. of oil lighter than and insoluble in water was obtained. At about 420°, 50% of the acetone was converted into an oil which was insoluble in water, and only a small percentage of the acetone was decomposed into carbon monoxide and methane. The liquid product distilled at 60–200°, combined with bromine, and decolorized potassium permanganate; its structure was investigated later (see below).

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[1] The curves are numbered according to the experiment.

Experiments 511, 512, 518, and 524 were made with the purpose of studying the catalytic reduction of acetone under the influence of iron. In Experiment 518 (Curve 518) the amount of isopropyl alcohol was determined. Forty grams of acetone was placed in the apparatus under an initial hydrogen pressure of 103 atmospheres. After 20 hours of heating, when equilibrium had been established, 37 g. (47 cc.) of liquid was obtained. Ten cc. of this liquid was insoluble in water; the remaining 37 cc. (31 g.) was passed slowly over alumina at 400°. Acetone at this temperature is unchanged whereas isopropyl alcohol is decomposed completely into propylene and water. The propylene was absorbed in bromine and the resulting propylene bromide (20 g.) distilled at 140–141°. About 20 g. of acetone was collected. Assuming that the product insoluble in water came from acetone, as indicated by Experiments 519–521, it might be inferred that about 25% of the original acetone under these conditions was reduced to isopropyl alcohol. This is the maximum yield of alcohol since under these conditions the reverse reaction also takes place, the dehydrogenation of isopropyl alcohol to acetone and hydrogen.

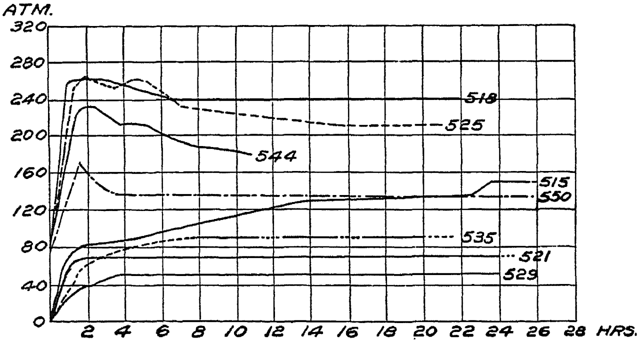


FIG. 21

Experiment 515 (Curve 515) showed that isopropyl alcohol decomposed under these conditions into acetone and hydrogen and that after a certain time an equilibrium was established; also, that the same amount of water-insoluble substance was formed as in the case of acetone. When 3 g. of reduced iron (from Kahlbaum) was introduced into the iron tube the course of the reduction changed very little as evidenced by the gas analysis and also from the amount of liquid product formed (Expt. 516). However, a larger amount of unsaturated hydrocarbon was obtained.

Hydrogenation of Isobutyraldehyde

Table 44 shows the results of a series of experiments on the hydrogenation of isobutyraldehyde.[1]

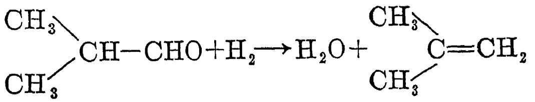
TABLE 44

CATALYTIC DECOMPOSITION AND HYDROGENATION OF ISOBUTYRALDEHYDE UNDER HYDROGEN PRESSURE IN THE PRESENCE OF IRON

Expt. No.	T., °C.	Press., Atms.			Time, Hrs.	Gaseous Products, Liters	Analysis of Gas, % by Vol.				
		Initial	Max.	Final (Room Temp.)			CO_2	C_nH_{2n}	CO	H_2	C_nH_{2n+2}
542 [a]	400	85	203	85	9	25.0					
529 [b]	400	0	61	4	28	1.6	0.2	1.0	19.2	5.5	22.4
531	400	0	88	21	24	7.4	2.6	0.6	51.2	2.6	40.8
535	400	0	99	26	23	9.1	3.0	0.8	46.8	5.6	43.6
532	350	0	42	1	3						
525	400	101	274	69	26	16.0					
550	360	100	170	61	26	15.8	2.6	0.4	17.4	50.8	26.4

[a] Copper catalyst.
[b] This experiment was on the decomposition of isobutanol.

Experiment 542 was made in order to determine whether hydrogen will add to ketones and aldehydes in the absence of an iron catalyst. A charge of 30 g. of isobutyraldehyde under 85 atmospheres of hydrogen was heated in a high pressure apparatus made of phosphor bronze which did not contain any iron. After heating for 9 hours the reaction product was removed. It was 75% unchanged aldehyde and 25% water and polymerization products of isobutylene, the latter being formed according to the following equation:



$$\left.\begin{array}{l}CH_3\\CH_3\end{array}\right\rangle CH{-}CHO+H_2\rightarrow H_2O+\left.\begin{array}{l}CH_3\\CH_3\end{array}\right\rangle C{=}CH_2$$

From the small fraction distilling at 100–115° it was impossible to isolate any isobutyl alcohol. After distilling off the aldehyde the chief fraction distilled at 115–116°. Thus, the addition of hydrogen to isobutyraldehyde in the presence of copper did not occur in spite of the high hydrogen pressure (200 atmospheres). In order to determine the products formed by heating isobutyl alcohol and isobutyraldehyde in an iron tube in the absence of hydrogen, Experiments 529, 531, 532, and 535 were made. Isobutyl alcohol (Expt. 529) at 400° yielded a considerable amount of polymerization products of isobutylene and a gas containing much carbon monoxide. At 350°, isobutyraldehyde decomposed very little, a small amount of condensation product and gas being obtained.

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[1] All the aldehydes studied were prepared by the catalytic decomposition of alcohols in a brass tube at ordinary pressure.

When isobutyraldehyde was heated in the iron tube under 100 atmospheres of hydrogen (Expts. 525–550) most of the aldehyde was converted into isobutyl alcohol. In Experiment 550 (Curve 550) it was found that the liquid product of the reaction contained only 2 g. of aldehyde, 75% of the liquid being isobutyl alcohol and the remainder condensation products of the isobutylene resulting from the decomposition of isobutyraldehyde. Consequently, isobutyraldehyde adds hydrogen and forms isobutanol in the presence of an iron catalyst.

Hydrogenation of Isovaleraldehyde

On heating isovaleraldehyde under hydrogen pressure in the presence of an iron catalyst, isoamyl alcohol was formed, the alcohol being accompanied by a certain amount of amylene that was produced chiefly by the decomposition of the aldehyde. Under these conditions isoamyl alcohol did not form amylene or its condensation products, except in very small amounts.

Thus the experiments on the hydrogenation of aldehyde and ketones in the presence of iron catalysts established the fact that these carbonyl compounds are converted into the corresponding alcohols. This hydrogenation occurs under a high pressure of hydrogen and at a certain temperature, and the reaction is reversible. My preceding experiments showed that in the presence of iron catalysts, hydrogenation of olefin hydrocarbons also takes place and that *non-reduced* iron has the same sort of catalytic effect as reduced nickel, the only difference being that a higher temperature is required with non-reduced iron than with nickel. We intended to test the catalytic activity of other metals of the iron

TABLE 45

HYDROGENATION OF ISOVALERALDEHYDE IN THE PRESENCE OF IRON

EXPT. No.	SUBSTANCE	CATALYST	T., °C.	INITIAL PRESSURE OF H_2, ATMS.	MAX. PRESS., ATMS.	FINAL PRESS., ATMS. (ROOM TEMP.)	TIME, HRS.	ANALYSIS OF GASES					GASEOUS PRODUCTS, LITERS
								CO_2	C_nH_{2n}	CO	H_2	C_nH_{2n+2}	
541	Isoamyl Alcohol	Fe	400	100	240	100	12		No decomposition				19.6
546	Isoamyl Alcohol	Fe	400	79	192	74	7		No decomposition				18.0
543	Isovaler-aldehyde	Fe	400	83	215	68	19	0.8		19.2	58.6	19.6	12.0
544	Isovaler-aldehyde	Fe	400	85	232	60	12			18.0	57.6	22.8	10.0

group—chromium and manganese—in the hydrogenation of aldehydes and ketones.

The Reversibility of Catalytic Hydrogenation in the Presence of Reduced Nickel

After the reversibility of the catalytic hydrogenation of aldehydes and ketones under the influence of iron had been proven, it was of interest to make a detailed study of the reversibility of hydrogenation in the presence of nickel under high pressure. The behavior of several substances was investigated.

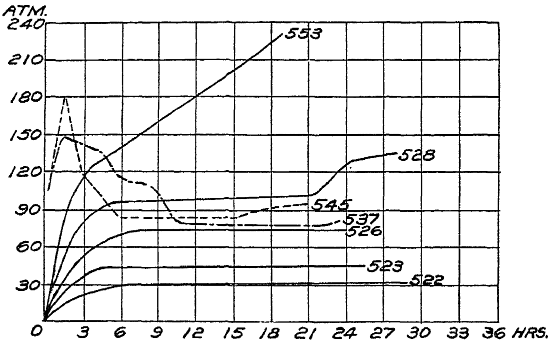

Fig. 22

Isopropyl Alcohol.—The data of Table 46 and Fig. 22 concern the catalytic decomposition of isopropyl alcohol at various temperatures (200–325°) under high pressure.

Forty grams of isopropyl alcohol was charged into the apparatus for each experiment and the apparatus was heated in an oven at a definite temperature. The experimental results of Experiments 522 and 523 (see table and diagram) lead to the conclusion that the decomposition of isopropyl alcohol in the presence of reduced nickel at 200–300° is a reversible reaction.

$$CH_3\text{—}CHOH\text{—}CH_3 \rightleftarrows CH_3COCH_3 + H_2$$

The reaction in spite of long heating comes to a standstill as evidenced by the attainment of a constant pressure, the products being acetone, hydrogen, and isopropyl alcohol. A small amount of saturated hydrocarbons (mostly methane) was also present in the gas due to a side reaction in the decomposition of the alcohol. The higher the temperature, the larger the quantity of acetone

TABLE 46

EXPT. No.	SUBSTANCE	CATALYST	T., °C.	INITIAL PRESS. OF H_2, ATMS.	MAX. PRESS., ATMS.	FINAL PRESS., ATMS. (ROOM TEMP.)	TIME, HRS.	ANALYSIS OF GASES				GASEOUS PRODUCTS, LITERS
								CO_2	C_nH_{2n}	H_2	C_nH_{2n+2}	
522	Isopropyl Alcohol	Red. Ni	200	0	28	11	33	0.2		93.8	5.3	2.1
523	Isopropyl Alcohol	Red. Ni	230	0	46	20	29	0.4		83.4	15.2	3.6
526	Isopropyl Alcohol	Red. Ni	260	0	73	30	25	1.6		58.3	39.7	5.6
528	Isopropyl Alcohol	Red. Ni	300	0	128	45	28	9.4	1.4	17.6	71.4	11.8
553	Isopropyl Alcohol	Red. Ni	325	0	230	77	24	13.4	0.6	19.0	6.10	22.0
537	Acetone	Red. Ni	250	100	152	32	21	1.0		61.8	3.27	7.5
545	Acetone	Red. Ni	250	111	181	38	23	0.6		58.1	4.71	9.1

produced from the isopropyl alcohol and, at the same time, the greater the amount of saturated hydrocarbons. Equilibrium was established only after a long time. Experiments 526–528 indicate that in spite of long heating, equilibrium had not yet been reached although the decomposition had almost ceased. Experiments show that there is a critical temperature for reduced nickel (about 300°) at which the decomposition of isopropyl alcohol changes in character to yield mainly water, saturated gaseous hydrocarbons, and a small amount of hydrogen. This critical temperature is much lower than that for iron catalysts in which case it was found to be around 570°. The property of reduced nickel which promotes the decomposition of alcohol into saturated hydrocarbons makes it unsuitable as a catalyst for the decomposition of alcohols into aldehydes and ketones. This fact was already indicated when I pointed out [1] the advantage of iron and zinc [2] for the production of aldehydes and ketones from alcohols.

When 40 g. of acetone and 2 g. of reduced nickel were heated in the high pressure apparatus in the presence of hydrogen at 250° (Expts. 537, 545) the same products were obtained (under the same conditions of time, pressure, and temperature) as when the starting material was isopropyl alcohol.

The reduction of acetone to isopropyl alcohol by hydrogen in the presence of nickel goes to completion only up to a certain temperature, about 210–220°. Above this temperature, at 220–230°, the reverse reaction (isopropyl alcohol decomposing into acetone and hydrogen) starts and part of the isopropyl alcohol decomposes into water and saturated hydrocarbons. Eventually, at these higher temperatures a condition of equilibrium becomes established as in the case of isopropyl alcohol. At 250° equilibrium is attained only after a very long time because of the slow decomposition of alcohol and probably also of acetone into water and saturated hydrocarbons. The descending branch, corresponding to the reduction of acetone, and the ascending branch, corresponding to the decomposition of alcohol formed, can be clearly distinguished on the curve.

Methylethyl Carbinol.—Secondary butyl alcohol (prepared in the high pressure apparatus by the reduction of methylethyl ketone by hydrogen in the presence of nickel) decomposed under the influence of the same catalyst in a manner similar to that of isopropyl alcohol. The only difference was that all the temperatures for methylethyl carbinol are slightly higher than those for isopropyl alcohol.

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[1] Ipatieff, J. Russ. Phys. Chem. Soc., *38* (1906); Chem. Zentr., 1906, II, 86.

[2] Ipatieff, Ber., *35*, 1947 (1902).

TABLE 47

DECOMPOSITION OF METHYLETHYL CARBINOL AND HYDROGENATION OF METHYLETHYL KETONE UNDER PRESSURE IN THE PRESENCE OF REDUCED NICKEL

SUBSTANCE	T., °C.	INITIAL PRESS. OF H_2, ATMS.	MAX. PRESS., ATMS.	FINAL PRESS., ATMS.	TIME, HRS.	GASEOUS PRODUCTS, LITERS	ANALYSIS OF GAS, % BY VOL.				
							CO_2	C_nH_{2n}	CO	H_2	C_nH_{2n+2}
Methylethyl Carbinol	300	0	83	22	5	5.0	1.9	1.5	0.5	62.0	22.0
Methylethyl Ketone	250	100	142	33	24	7.0				28.0	72.0

In the decomposition of methylethyl carbinol and the hydrogenation of methylethyl ketone equilibrium takes place at the temperatures indicated, and in each case the liquid products consist of a mixture of ketone and alcohol. The shape of the decomposition curves is similar to that for the decomposition of isopropyl alcohol.

Isoamyl Alcohol.—In order to compare the decomposition of primary alcohols with that of secondary alcohols under the influence of nickel, an experiment was made on the reduction of isovaleraldehyde in the presence of nickel and excess hydrogen. The data show that equilibrium was reached at 250°. The liquid products consisted chiefly of alcohol and a small amount of aldehyde; the gas was mostly hydrogen. This reaction is also reversible. It is to be noted that primary alcohols decompose under the influence of nickel into water and saturated hydrocarbons at a higher temperature than do secondary alcohols.

Methyl Alcohol.—By heating methyl alcohol with excess hydrogen at high pressure and temperature in the presence of reduced nickel one would expect to obtain methane and water as reaction products since all the possible products of decomposition would be reduced to methane under the conditions of the experiment.

(1) $CH_3OH \rightarrow HCHO + H_2$ (2) $HCHO \rightarrow H_2 + CO$
(3) $CO + 3H_2 \rightarrow CH_4 + H_2O$ (4) $CH_3OH + H_2 \rightarrow CH_4 + H_2O$

It was always noticed that a part of the methyl alcohol remained undecomposed. Experiments carried out later by me,[1] as well as by Razuvaev, showed that we were dealing with a reversible reaction: water oxidizing methane to carbon dioxide.

$$CH_4 + 4H_2O \rightleftarrows CO_2 + 4H_2$$

HYDROGENATION IN THE PRESENCE OF METAL OXIDES

After I had discovered the catalytic decomposition of alcohols [2] into aldehydes (or ketones) and hydrogen the fact was established that certain oxides could accomplish the same result. For instance, although ordinary metallic tin and copper do not promote the dehydrogenation of alcohols, this reaction is readily brought about in the presence of the oxides of these metals. When alcohol vapor is passed over these oxides,[3] reduction takes place with the formation of highly dispersed metal and it is the latter which promotes the dehydrogenation.

After this work,[4] my attention was again centered on the study of catalytic hydrogenation under the influence of metal oxides. This investigation was undertaken for the purpose of obtaining experimental evidence capable of explaining the catalytic reactions of hydrogenation and dehydrogenation, i.e., of reduction and oxidation processes.

A description of the experiments which were carried out with the black and green oxides of nickel on the hydrogenation of many organic compounds in the high pressure apparatus will be given. In all cases 25 g. of the organic compound and 2 g. of commercial oxide or sub-oxide were placed in the apparatus, the organic compound being added first. The manner in which the nickel oxide was added markedly influenced the velocity of the reaction as is evident from the experimental data. Finally, dry hydrogen was pumped into the apparatus up to 100–120 atmospheres and the apparatus was heated in an electric furnace at 200–250°.

In Table 49 and the accompanying Fig. 24 are summarized the experimental data on the hydrogenation of benzene in the presence of nickel oxide, nickel sub-oxide, and nickel reduced at 270° at ordinary pressure.

It is seen that at 250° the hydrogenation of benzene in the presence of nickel oxide takes place at high velocity. The value $(dP/dT)_{\max}$ for nickel oxide which serves as a measure of the highest

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[1] Ipatieff, J. prakt. Chem., *87*, 479 (1912).

[2] Ipatieff, Ber., *34*, 3579 (1901).

[3] Ipatieff, Ber., *34*, 152 (1902).

[4] Ipatieff, Ber., *40*, 1281 (1907).

TABLE 48

Expt. No.	Substance	Catalyst	T., °C.	Initial Press. of H_2, Atms.	Max. Press., Atms.	Final Press., Atms. (Room Temp.)	Time, Hrs.	Analysis of Gases, % by Vol.				Gaseous Products, Liters
								CO_2	CO	H_2	C_nH_{2n+2}	
539	Valeric Aldehyde	Ni	250	129	185	65	24	0.6	0.2	82.4	16.9	14.3
533	Methyl Alcohol	Ni	386	101	325	105	3.5	3.6		71.3	25.1	23.8
534	Methyl Alcohol	Ni	400	70	252	77	23	5.6		50.9	43.9	18.0
538	Methyl Alcohol	Ni	450	60	201	50	11	1.6		57.8	40.9	14.7

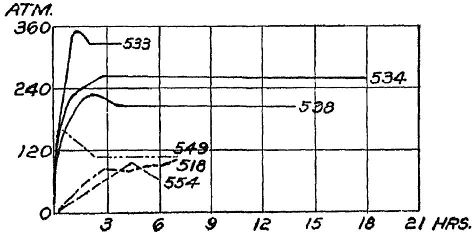


Fig. 23

TABLE 49

HYDROGENATION OF BENZENE (25 G.) UNDER PRESSURE IN THE PRESENCE OF NICKEL OXIDES, REDUCED NICKEL, AND IRON

EXPT. No.	CATALYST	T., °C.	INITIAL PRESS. OF H_2, ATMS.	MAX. PRESS., ATMS.	FINAL PRESS., ATMS. (ROOM TEMP.)	TIME, HRS.	ANALYSIS OF GASES		$\left(\frac{dP}{dT}\right)_{max}$
							H_2	CH_4	
561	NiO, Black	250	120	180	11	2.25	Hydrogen		4.0
562	NiO, Black	252	120	184	11	3.25			4.6
564	NiO, Used Once	250	120	169	11	2.25			4.0
565	NiO, Green	250	120	195	20	3.00			3.0
568	NiO, Black	260	120	186	11	2.25			7.0
574	NiO, Black	255	120	182	12	2.25			6.6
578	NiO, Black	290	120	180	26	4.00	45.5	54.5	5.8
571	NiO, Used Twice	282	120	167	11	4.50	Hydrogen		2.2
576	NiO, Black	200	120	179	13	6.00	Hydrogen		1.9
582	NiO, Green	200	120	179	15	12.00	Hydrogen		0.4
572	NiO, Below the Benzene	250	120	182	25	10.33	Hydrogen		1.4
567	Reduced Ni, Below the Benzene	254	115	157	19	9.00			1.8
570	Reduced Ni, Above the Benzene	255	107	156	10	3.50			2.8
573	Reduced Ni, Above the Benzene	250	118	166	19	3.00			2.6
575	Reduced Ni, Shaken Down	250	105	158	10	4.00			2.0
581	Fe	255	110	184	110	13.00	Hydrogen		
579	0.5 g. NiO, Black	250	115	180	19	6.00			1.2
580	0.1 g. NiO, Black	242	112	165	12	6.00			0.7
584	0.001 g. NiO	250	108	181	104	25.00			
587	0.02 g. NiO	250	105	189	61	100.0			

speed of this reaction, reaches a considerable value, 6–7 k.m., which exceeds several times the magnitude of $(dP/dT)_{\max}$ for reduced nickel. In Experiments 561, 562, 568, and 574, where such a high speed of the reaction was developed, nickel oxide was placed in the tube of the apparatus after the benzene had been added. Curve 561 presents graphically the course of the reduction. If we exclude the time required to heat the apparatus to 250°, then the entire hydrogenation took place in one and a half hours, and cyclohexane was obtained in theoretical yield (without a trace of benzene as shown by the test with nitrating mixture). Such a speed of hydrogenation in the presence of nickel oxide exceeds several times that obtained according to the method of Sabatier and Senderens. Moreover, their product was always contaminated with a certain amount of benzene which necessitated subsequent purification with resultant loss of product.

At the end of the reaction, it was advantageous to decrease the temperature slightly (about 15–20°) so that the cyclohexane would not decompose under the lower hydrogen pressure. At 250° hydrogenation under high hydrogen pressure proceeds without decomposition, but at higher temperatures such as 290° (Expt. 578), in spite of the excess of hydrogen and the pressure, cyclohexane began to decompose into methane, benzene, and carbon to an appreciable extent.

When the temperature of hydrogenation was 200° the reaction velocity dropped considerably and also the value $(dP/dT)_{\max}$ decreased to approximately one-third of the value at the higher temperature (Expt. and Curve 576). When, instead of nickel oxide, nickel sub-oxide (commercial, obtained by precipitation with alkali and not very strongly ignited) was used (Expt. 565), hydrogenation was faster than with reduced nickel but slower than with nickel oxide.

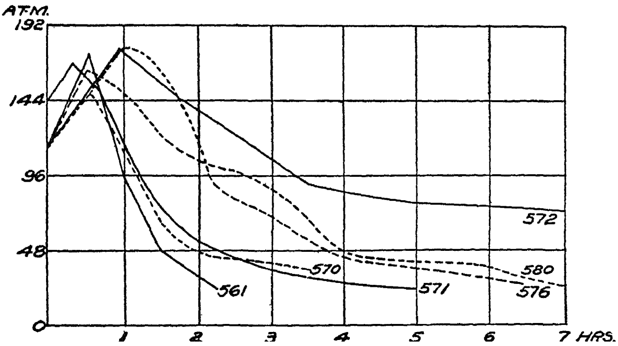


FIG. 24

Nickel oxide can be washed with ether after participating in the hydrogenation reaction and used again with practically the same catalytic activity (Expt. 564). However, after using it a second time it had lost some of its catalytic activity (Expt. and Curve 57), and the reaction velocity approached that for hydrogenation with reduced nickel. Experiments with nickel reduced at ordinary pressure and at 270° (Expts. 570–572 and Curve 570) gave a value for $(dP/dT)_{\max}$ of about 2.7 k.m., when the nickel was above the benzene. However, when the nickel oxide (Expt. and Curve 572) or the reduced nickel (Expt. 567) was put into the apparatus before the benzene the velocity of hydrogenation dropped suddenly and the value of $(dP/dT)_{\max}$ in both cases was about 1.6 k.m.

When the order of addition was benzene, reduced nickel, and hydrogen, followed by shaking the contents of the apparatus, the velocity of hydrogenation (Expt. 575) was high and approached that observed when nickel was introduced into the tube after pouring in the benzene. The influence of the order of addition of the catalyst upon the velocity of the hydrogenation of benzene might be explained by the fact that the walls of the tube were wet with benzene and were also covered with nickel oxide in the fast reactions. This distribution of catalyst was more effective than when it was at the bottom of the tube in a pile.

As seen from Table 49, the velocity of the hydrogenation reaction diminishes considerably with decrease in the amount of catalyst. A twenty-fold decrease in catalyst triples the time necessary for the reaction (Expt. and Curve 580). By decreasing the amount of catalyst to one-hundredth of the original amount (Expt. 587), the time required was increased 40–45 times and even then the reaction was not complete, the product containing only 40% of cyclohexane. When only one two-hundredth of the usual amount of catalyst was taken (Expt. 581) the reaction proceeded hardly at all. Experiment 581, without catalyst, was made so as to be sure that the apparatus was clean and did not contain nickel oxide.

Experiments on the hydrogenation of benzene in the presence of nickel oxide under high pressure of hydrogen plainly show the superiority of nickel oxide over reduced nickel. With the oxide the reaction was not only faster but the product was of better quality.

The latter circumstance might be explained by the fact that reduced nickel partially decomposes cyclohexane at this temperature into methane and benzene, whereas nickel oxide is not able to effect this decomposition. But if we assume that a part of the nickel oxide is reduced to nickel under high pressure, the experiments show that only very little metallic nickel can be present, else decomposition of cyclohexane would take place.

With these conceptions in mind, I studied the action of nickel oxide upon a series of organic compounds many of which could not be hydrogenated at all at ordinary pressure.

In the following table are given data concerning the hydrogenation of a number of organic compounds.

Nickel oxide is a more effective catalyst for the hydrogenation of

TABLE 50

HYDROGENATION OF ORGANIC COMPOUNDS UNDER PRESSURE IN THE PRESENCE OF NICKEL OXIDE (BLACK)

Expt. No.	Substance	T., ° C.	Press., Atms.			Time, Hrs.	Product
			Initial of H_2	Max.	Final		
569	Acetone, 40 g.	250	107	181	28	6	Pure isopropyl alcohol
563	Phenol, 25 g.	245	120	189	18	14	Cyclohexanol
588	Diphenyl, 20 g.	260	120	191	36	12	Dicyclohexyl
589	Naphthalene, 15 g.	260	121	181	80	24	Tetrahydronaphthalene
601	Tetrahydronaphthalene, 22 g.	230	110	178	62	12	Pure decahydronaphthalene
590	Benzil, 15 g.	260	120	192	68	9	Pure dicyclohexylethane
597	β-Naphthol, 20 g.	225	125	191	40	72	β-Decahydronaphthol
596	α-Naphthol, 20 g.	230	117	112	34	72	α-Decahydronaphthol
609	β-Naphthol, 20 g.	230	120	191	50	56	β-Decahydronaphthol
612	α-Naphthol, 20 g.	225	115	168	51	72	α-Decahydronaphthol
592	Benzophenone, 15 g.	260	105	188	81	28	Diphenylmethane

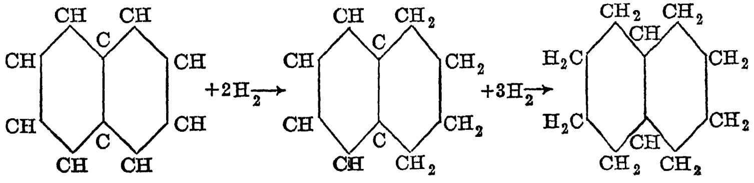
acetone to isopropyl alcohol than reduced nickel (Expt. 569). The same is true for the hydrogenation of phenol to cyclohexanol (Expt. 563).

Dicyclohexyl.—The hydrogenation of diphenyl, $C_6H_5—C_6H_5$, in the presence of nickel oxide (Expt. 588), yielded dicyclohexyl, $C_6H_{11}—C_6H_{11}$. The product distilled at 240–241° and solidified to a crystalline mass when the receiver was cooled in snow. A test with nitrating mixture (one part HNO_3 [*d*, 1.5] and three parts H_2SO_4 [*d*, 1.84]) showed the absence of even traces of aromatic hydrocarbons. The calculated amount of hydrogen, based on complete hydrogenation of diphenyl, was absorbed. By this method it is very easy to obtain pure dicyclohexyl.

Anal. Calcd. for $C_{12}H_{22}$: C, 86.7; H, 13.3. Found: C, 86.2; H, 13.5.

Tetrahydronaphthalene and Decalin.—For the hydrogenation of naphthalene, material was used which had not been especially purified. Hydrogenation gave a liquid product (Expt. 589) boiling at 208–212°. According to its analysis and properties this product was tetrahydronaphthalene.

Anal. Calcd. for $C_{10}H_{12}$: C, 90.9; H, 9.1. Found: C, 91.0; H, 9.3.



This hydrocarbon doubtless still had an aromatic nucleus since it reacted violently with nitrating mixture. But in spite of long heating, hydrogenation stopped at this stage and in order to obtain a product of higher degree of hydrogenation it was necessary to subject this hydrocarbon again to hydrogenation with nickel oxide and hydrogen (Expt. 601) at 230°. The product from the second hydrogenation boiled at 189–191°. It did not react with strong sulphuric acid nor with nitrating mixture and it did not oxidize on standing in air. Analysis confirmed the formula $C_{10}H_{18}$.

Anal. Calcd. for $C_{10}H_{18}$: C, 86.9; H, 13.2. Found: C, 87.4; H, 13.4.

Thus, the hydrocarbon boiling at 189–191° represents the product of complete hydrogenation of naphthalene, i.e., decahydronaphthalene (decalin).

Dicyclohexylethane.—In the presence of nickel oxide it is very easy to obtain dicyclohexylethane from benzil and hydrogen (Expt. 590).

$$C_6H_5—CO—CO—C_6H_5 + 10H_2 \longrightarrow C_6H_{11}—CH_2—CH_2—C_6H_{11} + 2H_2O$$

The amount of hydrogen consumed corresponded to the complete hydrogenation of benzil. Dicyclohexylethane is a liquid boiling at 274–275.5°. It did not solidify at 0°, its odor was agreeable, it did not decolorize permanganate, nor did it react with nitrating mixture.

Anal. Calcd. for $C_{14}H_{26}$: C, 86.6; H, 13.4. Found: C, 85.9; H, 13.3.

The yield of dicyclohexylethane was excellent (12 g. from 15 g. of benzil).

Beta-Decahydronaphthol.—The hydrogenation of beta-naphthol, $C_{10}H_7OH$, in the presence of nickel oxide (Expts. 597 and 609) yielded a liquid which boiled at 210–250°, chiefly at 242–244°. This latter fraction was a very thick liquid with an odor of mint which on long standing deposited crystals melting at 99–100°. Analysis of the liquid of boiling point 242–244°, as well as of the crystalline substance, confirmed the formula $C_{10}H_{17}OH$.

Anal. Calcd. for $C_{10}H_{17}OH$: C, 77.8; H, 11.7. Found: (Liquid) C, 78.0; H, 11.7; (Solid) C, 77.4; H, 11.8.

The substance liberated hydrogen when heated with metallic potassium and reacted with phosphorus pentachloride; accordingly it can be considered as beta-decahydronaphthol.

Alpha-Decahydronaphthol.—Hydrogenation of alpha-naphthol in the presence of nickel oxide yielded alpha-decahydronaphthol (Expts. 596–612) but only in a small yield. The greater part of the alpha-naphthol was reduced to a hydrocarbon with elimination of water. Therefore, the hydrogenation of alpha-naphthol must be conducted at the lowest possible temperature. Decahydronaphthol was obtained first as a thick liquid with a boiling point of 245–250° which after a time deposited crystals melting at 57–59°.

Anal. Calcd. for $C_{10}H_{17}OH$: C, 77.8; H, 11.7. Found: C, 77.9; H, 12.0.

There was also obtained in this reaction a considerable quantity of liquid boiling at 200–220°, which was not further investigated.

Diphenylmethane.—Diphenylmethane, $C_6H_5—CH_2—C_6H_5$, was obtained by the complete hydrogenation of benzophenone in the presence of nickel oxide (Expt. 592). This experiment, as well as the preceding ones, showed that high pressure hydrogenation reduced hydroxylated side chains and carbonyl groups to hydrocarbon. With special precautions a carbonyl compound can be hydrogenated to the corresponding alcohol, e.g., if the reaction is carried out in solution.

THE RÔLE OF OXIDES IN CATALYSIS

After it was proven that the catalytic reactions of dehydrogenation and hydrogenation proceed in the presence of metal oxides, it seemed interesting to determine the fate of these metal oxides and especially of nickel oxide in high pressure hydrogenation. It might be supposed that under the high pressure of hydrogen, nickel oxide would be reduced to nickel, the latter serving as catalyst. But analysis of the oxide and sub-oxide of nickel taken from the apparatus after hydrogenation showed that if reduction of nickel oxide had taken place, it was insignificant in amount. To understand the rôle of the nickel oxide catalyst it was necessary to determine accurately the extent of reduction. The desire to understand the nature of the catalyst occasioned the study of the hydrogenation of numerous compounds under a variety of conditions. It also appeared necessary to study the effect of nickel oxide and of reduced nickel upon the formation of water. This necessitated a rather detailed study since there were but few data in the literature and the experiments of Moissan[1] upon the reduction of nickel oxide led to erroneous conclusions.

Before I describe my experiments, I will mention the most important experiments that had previously been made on the reduction of nickel oxides by hydrogen. Müller[2] first investigated the reduction of nickel oxide. Moissan, the last investigator of this reaction, did not prove the existence of Ni_2O; in fact he did not mention the previous work of Müller, but he indicated that the reduction of nickel oxide can go in steps. At 190°, nickel oxide (Ni_2O_3) is converted quantitatively into the magnetic oxide, Ni_3O_4. When the temperature is raised to 200°, the green or yellow sub-oxide (NiO) is formed. At 200° this sub-oxide is stable, but at 230–240° it is reduced to nickel which is pyrophoric at ordinary temperature, igniting in the air to give Ni_2O_3. Moissan concluded that the ignition temperature of nickel is not high since the only oxide stable at high temperature is the sub-oxide, NiO. The sub-oxide as obtained by reduction with hydrogen is a green powder at ordinary temperature. It absorbs oxygen readily from the air, becomes black, and increases in weight. A characteristic property of the sub-oxide is its easy oxidation. At 355–440° it changes into Ni_2O_3, but above 440° the latter starts to decompose and at 600° the sub-oxide is again obtained. In other words the higher oxides can exist only at definite temperatures. The above are the essential data on the reduction of nickel oxide with hydrogen.

I received the following analytical data on nickel oxides obtained from Kahlbaum. The nickel content was determined by electrolysis, this method being preferable to the determination of nickel as sub-oxide.

It is evident that the so-called "nickel oxide" obtained from Kahlbaum contains much more nickel than required by the formula Ni_2O_3 (71% of Ni). It should be noted also that the samples of nickel oxide obtained from Kahlbaum at different times contained different amounts of nickel. When I communicated with Kahlbaum I received the answer that the nickel content as determined by me coincided completely with their analyses and that it was impossible to prepare commercially a nickel oxide containing the theoretical percentage of nickel. In one of the last samples the nickel content reached 78.8% which corresponds to

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[1] Moissan, Ann. chim. phys., *5*, 21 (1880).

[2] Müller, Pogg. Ann., 136 (1869).

TABLE 51

Nickel Oxide	Color of Nickel Oxide	Drying T., °C.	Amount of Moisture, %	% Content of Ni in the Dried or Crude Oxide
NiO	Green	110		77.47
NiO, Chemically Pure	Green	600		79.3
Ni_2O_3	Brownish	Not dried		72.36
Ni_2O_3	Brownish	Dried in the apparatus at 170–180		73.00
Ni_2O_3	Brownish	170–180 Pressure		74.40
Ni_2O_3	Brownish	170–180	2.77	74.60
Ni_2O_3	Brownish	190–200	2.85	74.92
Ni_2O_3	Brownish	250	2.92	
Ni_2O_3	Brownish	525		76.0
Ni_2O_3	Brownish	Ignited on the soldering bench	6.5	77.64
Ni_2O_3, Chemically Pure	Black	Not dried		74.20
Ni_2O_3, Chemically Pure	Black	130–140		74.88
Ni_2O_3, Chemically Pure	Black	140		74.98
Ni_2O_3, Chemically Pure	Black	170–180	0.45	75.27
Ni_2O_3, Chemically Pure	Black	Ignited by blast-lamp	6.1	76.18
Ni_2O_3, Ordinary	Black	Not dried		78.78
Ni_2O_3, Ordinary	Black	Not dried		78.56

the formula NiO, but it should be mentioned that the color of the nickel oxide was black.

When nickel oxide is heated above 120°, separation of water is observed, the amount increasing with rise of temperature and the nickel content of the remaining oxide is considerably higher than that in the original sample. When nickel oxide is strongly ignited (by a blast lamp) about 6% of water is eliminated but the final nickel content does not reach that of the sub-oxide (78.6%). In order to determine more accurately the amount of water present in nickel oxide and also to determine whether oxygen separates from nickel oxide, and how much, several experiments were made in high melting glass tubes, the water being absorbed in two calcium chloride tubes. In most of the experiments dry air was passed through the tube, and the exit air, together with the oxygen liberated from the oxide, was collected in a gasometer and analyzed. Knowing the amount of air used, the oxygen liberated could be calculated. The data are shown in the following table. Black nickel oxide (71.8% nickel) was used.

TABLE 52

Amt. of NiO, G.	T., °C.	Time		Amt. of Water, G.	Amt. of Water, %	Amt. of Oxygen, Cc.	Percentage Nickel in the Ignited Product
		Hrs.	Min.				
6.4884	760	3	00	0.387	5.98		78.34
3.6418	210	9	00	0.0602	1.65		73.29
5.4196	750	3	00	0.3196	5.89	80	78.36
5.5070	750	3	00	0.334	6.06	80	78.35
5.0688	340–450	4	45	0.2942	5.8	23	78.18
5.1982	750	3	00			60	78.29
5.1970	500–550	3	45	0.3076	5.91	40	78.19

The data show that nickel oxide contains up to 6% of water which is removed when the oxide is heated above 300°, the last traces of water being eliminated only at high temperatures. If we make a calculation as to how much nickel is contained in the dry nickel oxide, we obtain 76.4% Ni.

If we assume that this oxide is a mixture of oxide and sub-oxide, calculation shows that not more than 25% of nickel oxide is present. If we calculate the amount of oxygen which will be obtained by conversion of nickel oxide into sub-oxide at 750°, taking into consideration that only 25% of nickel oxide is present, and then compare this amount with that actually obtained, we see that the actual amount of oxygen is only 50% of the calculated. This led us to believe that the nickel oxide content of commercial oxide is even smaller than 25% and it makes it seem doubtful that Ni_2O_3 is actually present.

All data indicated that commercial oxide contains very little Ni_2O_3 and that the oxide consists chiefly of sub-oxide, NiO, and a certain amount of firmly held water. There is no evidence that these two oxides, Ni_2O_3 and NiO, combine to form complex oxides such as Ni_3O_4. Turning now to the work of Moissan, we see that he made a serious mistake when he did not analyze his starting material, nickel oxide. Therefore, his conclusions from the reduction experiments lose their significance.

Moissan obtained various reduction products of nickel oxide by means of hydrogen but he did not study the problem with sufficient care. In dealing with the various reduction stages of a metal oxide it is not enough to determine only the metal content. It is necessary to have a qualitative reaction which, although not capable of distinguishing the stages, can show the smallest trace of reduced nickel. From the beginning of my work I used such a test, the reagent being nitric acid (*d*, 1.38–1.40) free from oxides of nitrogen. Many experiments convinced me that the least trace of reduced nickel made itself evident when such nitric acid was poured over it, red nitric oxide appearing in the cold or on warming in a water bath. Neither the sub-oxide nor the commercial oxide [1] caused the evolution of nitric oxide when treated with this nitric acid, even on heating. The use of this reagent is a reliable qualitative test for reduced nickel and the depth of color gives some indication of the amount present.

Experiments on the reduction of nickel oxides by hydrogen were carried out at ordinary pressure and under high pressure (in the high pressure apparatus). In one set of experiments at ordinary pressure, a weighed amount of oxide was placed in a glass tube through which hydrogen (dried and purified) was passed; the eliminated water was absorbed in calcium chloride and weighed. In the more accurate experiments, about 1 g. of nickel oxide was placed in a short glass tube (about 12 cm. long) fitted with a ground glass stopper. A long delivery tube with ground glass joint served for the introduction of hydrogen and the reduced product could be weighed without coming in contact with air. Constant temperature was ensured by placing the tube in a long gas-heated furnace, the portion of tube containing the oxide being in the middle of the furnace. The data are summarized in the following tables.

From these experiments, it is evident that reduction of nickel oxide begins at 170°, a very small amount of reduced nickel being present in the product, the increase in the nickel content being occasioned chiefly by the removal of the water originally contained in the nickel oxide. At 190° there is considerable reduction of nickel oxide and when the amount of nickel oxide used was small (Expts. 6, 7, 8), the product contained approximately the percentage of nickel corresponding to nickel sub-oxide. Oxides of nitrogen were abundantly produced in the cold when the product was treated with nitric acid which was evidence for the presence of con-

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[1] One sample of nickel oxide from Kahlbaum (Ni, 78.56%) contained reduced nickel according to this test and also one sample of nickel sub-oxide.

TABLE 53

REDUCTION BY HYDROGEN OF BROWNISH NICKEL OXIDE CONTAINING 72.56% NICKEL

EXPT. NO.	OXIDE	AMT. OF OXIDE, G.	T., °C.	TIME		AMT. OF WATER, G.	% OF NICKEL	FORMATION OF NITROGEN OXIDES
				Hrs.	Min.			
1	Ni_2O_3		172	4	00		74.40	Scarcely noticeable appearance of nitrogen oxides
2	Ni_2O_3 Dried at 120°	6.5	172	4	00	0.1292	74.60	
3	Ni_2O_3 Dried at 120°	6.25	180	4	00	0.144	75.66 75.72	Traces of nitrogen oxides
4	Ni_2O_3 Dried at 120°	6.63	190	4	00	0.172	74.76	
5	Ni_2O_3 Dried at 120°	4.8	190	4	00	0.121	74.39	Traces of nitrogen oxides
6	Ni_2O_3 Dried at 120°	1.1924	190	3	30	0.048	77.51	Appearance of nitrogen oxides in the cold
7	Ni_2O_3 Dried at 120°	1.123	190	4	30	0.058	78.21	
8	Ni_2O_3 Dried at 120°	1.0496	195	4	00	0.056	79.00	
9	Ni_2O_3 Dried at 120°	7.0	200	4	00	0.496	77.19	Appearance of nitrogen oxides
10	Ni_2O_3 Dried at 120°	7.0	212	4	00	0.582	78.98	
11	Ni_2O_3 Dried at 120°	2.06	270	4	00	0.5308	91.70	Decided formation of nitrogen oxides
12	NiO	6.78	200	4	00	0.02	78.6	No oxides of nitrogen

siderable reduced nickel. These first experiments therefore showed me that at 190° the reduction proceeds much further than the formation of magnetic oxide (Ni, 73.45%) and consequently the conclusion of Moissan that only magnetic oxide is formed at this temperature does not correspond with the facts. It is remarkable that commercial nickel sub-oxide is not reduced to nickel at 200° (Expt. 12), but in spite of long heating the product did not show even traces of nitrogen oxides on treatment with nitric acid.

The second series of experiments (Table 54) was carried out with chemically pure but undried nickel oxide (from Kahlbaum), which was black in color and contained 74.20% of nickel.

On drying at 170–180°, 0.4% of water was removed from this nickel oxide. Reduction of chemically pure nickel oxide also starts at 170°, a very small amount of reduced nickel being formed. At 190°, in spite of long heating, reduction does not go beyond a certain limit. According to Moissan, at this temperature only magnetic oxide is formed but we see that the percentage of nickel

TABLE 54

Expt. No.	Oxide	Amt. of Oxide, G.	T., °C.	Time, Hrs., Min.	Amt. of Water, G.	% of Nickel	Formation of Nitrogen Oxides
1	Ni_2O_3	1.3470	171	7:45	0.005	75.28	Traces
2	"	1.1614	180	3:30	0.0114	75.80	Traces
3	"	1.2434	190	3:30	0.082	77.10	More than traces
4	"	1.0806	190	9:45	0.073	77.04	More than traces
5	"	1.0656	190	10:00		77.60	More than traces
6	"	1.3948	200	3:45		77.22	More than traces
7	"	0.9992	200	10:00	0.1272	80.59	Moderate
8	"	1.1052	200	4:00	0.094	77.32	More than traces
9	"	1.0056	200	9:30	0.132	81.6	Moderate
10	"	1.0188	200	4:00	0.163	77.33	More than traces
11	"	1.5424	210	3:30	0.116	81.03	Moderate
12	"	1.3568	210	10:00	0.354	85.8	Moderate
13	"	1.5716	220	3:45	0.2524	88.56	Considerable
14	"	1.3856	230	3:30	0.3164	95.2	Very considerable
15	"	1.4432	280	3:45	0.3536	98.1	Very considerable
16	NiO Not Dried	1.0092	200	4:00		79.5	Traces
17	NiO Ignited	1.0608	220	4:00		80.24	Traces
18	NiO Not Dried	1.4742	220	4:30		85.80	Moderate
19	NiO	1.6380	280	3:45	0.39	95.17	Very considerable

is considerably more than that required by the formula $NiO \cdot Ni_2O_3$, and that the reduction product consists of a mixture of Ni, NiO, and Ni_2O_3. Four hours' reduction at 200° does not alter the product formed at 190°; only by heating for 9–10 hours is further reduction obtained, the product then containing slightly more nickel than the sub-oxide, the composition being Ni, NiO, and Ni_2O_3. Only when heated above 210° does the product contain 95.6% of nickel. Even at 280–300° pure nickel is not obtained, the purity being 98.1%.

Turning our attention to the reduction of nickel sub-oxide containing traces of reduced nickel (it gave nitrogen oxide when heated with nitric acid and the nickel content was 79.2%) we found that the reduction of nickel sub-oxide starts only above 200°. This fact answers the original question why the reduction of so-called nickel oxide does not proceed beyond a certain point at 200°. NICKEL OXIDE IS REDUCED TO NICKEL BY HYDROGEN AT 190–200° AND ORDINARY PRESSURE WHEREAS THE NICKEL SUB-

OXIDE PRESENT IN COMMERCIAL OXIDE IS NOT REDUCED UNDER THESE CONDITIONS.

Besides this, the inability of the sub-oxide present in commercial nickel oxide to be reduced by hydrogen at a temperature below 200° indicates that it possesses properties close to those of the green nickel sub-oxide obtained by igniting the hydrate of nickel sub-oxide.

It is interesting to note that when the green sub-oxide is strongly ignited it loses to a great extent its capacity for reduction by hydrogen at ordinary pressure. Ignition considerably raises the temperature of reduction.

We will now turn to the discussion of the experiments on the oxidation of reduced nickel and nickel oxides. On removing reduced product from the apparatus where the reduction was made and bringing it in contact with air, a rapid oxidation may occur and in some cases, depending upon the temperature of reduction, considerable heat is liberated and the powder may start to burn. Such pyrophoric properties belong only to products obtained below 270° and they must be ascribed to reduced nickel only. In order to determine the end product of this pyrophoric oxidation the following experiments were made.

TABLE 55

Amt. of Ni_2O_3, G.	T., °C.	Time, Hrs.	Amt. of Water H_2O, G.	% of Ni in the Reduced Product	% of Ni in the Product after Standing in Air
0.8380	200	4	0.067	77.32	77.30
0.9816	210	4	0.176	81.03	80.36
1.0808	230	4	0.244	95.20	82.00
	270–280			98.2	97.54

As seen from the above data, nickel does not oxidize to pure nickel oxide as thought by Moissan, but only to nickel sub-oxide and probably only superficially. Beneath the coating of oxide there is doubtless unoxidized nickel since all these products liberate nitrogen oxides when treated with nitric acid.

A series of experiments was made to determine the temperature at which the oxidation of reduced nickel and of nickel sub-oxide occurs. The results are summarized in Table 56.

Oxidation was brought about with dry air and also with moist oxygen, these gases being passed over the substance which was

TABLE 56

Expt. No.	Substance	Amt. of Substance, G.	Oxidant	T., ° C.	Time		Wt. of Substance after Oxidation, G.	% of Ni in the Oxidation Products	Formation of Nitrogen Oxides
					Hrs.	Min.			
1	Reduced Ni	1.6826	Dry air	170–180	4	30	1.6811	95.47	Violent
2	Reduced Ni	1.2734	" "	210–220	4	00	1.2758	95.4	"
3	Reduced Ni	1.0462	" "	270–280	3	40	1.0864	95.30	"
4	Reduced Ni	1.0052	" "	350–360	3	40	1.1444	82.80	Moderate
5	Reduced Ni	1.0624	" "	400	5	00	1.2654	78.15	No liberation
6	Reduced Ni	1.1708	" "	400	5	30	1.4124	77.99	No liberation
7	Reduced Ni	1.0014	" "	445	5	00	1.1998	77.89	No liberation
8	Reduced Ni	0.9084	Dry oxygen	300	5	00	0.9332	94.7	Violent
9	Reduced Ni	1.3876	Dry oxygen	380	5	00	1.642	78.63	Traces
10	Reduced Ni	0.9232	Moist oxygen	300	5	00	1.0970	81.25	Moderate
11	Reduced Ni	1.0144	Oxygen at and afterwards hydrogen at	400 300	4 4	00 00	0.9812	95.23	Violent
12	NiO	1.1120	Dry air	360	3	30		79.50	Traces
13	NiO	0.9492	" "	410	3	30	0.9426	79.28	"
14	NiO	1.0656	" "	425	4	30	1.055	79.20	"
15	NiO	0.9440	Oxygen	425	4	30	0.9416	79.14	"
16	NiO	0.9712	"	480	4	30	0.9716	79.11	"
17	NiO	0.9840	Moist oxygen	420	5	00	0.9970	79.13	"
18	NiO	1.0364	Dry oxygen	220	3	20	1.0319	79.22	
19	NiO contains 1.7% H_2O	5.0822	Dry air	440–500	5	30		78.19	No liberation
20	NiO contains 1.7% H_2O	5.1216	" "	440–480	3	10		78.03	No liberation

placed in the previously described apparatus for the reduction of the nickel oxides. In Expts. 12–18 the reduced nickel contained 97.54% of nickel and the sub-oxide contained 79.30%; in Expts. 19–20 the sub-oxide contained 76.85% of nickel, and in addition, 1.7% of water since it had not been ignited.

The following conclusions may be drawn from the above data: (1) nickel reduced at 270–280° is oxidized by dry air and oxygen at about 350°; (2) at 400° nickel is oxidized almost completely to nickel sub-oxide (if the content of nickel in the product is insufficient for the formula NiO, this may be explained either by the retained water or by the formation of small amounts of higher oxides of nickel); (3) Expt. 11 shows that after being oxidized by oxygen at 400°, the product can be reduced again by hydrogen at 300° to the original product; (4) water plays an important part in the oxidation of reduced nickel, Expt. 10 showing that nickel is oxidized by moist oxygen at 300°, while dry oxygen at this temperature does not act upon it (Expts. 3 and 8); (5) nickel sub-oxide [1] is not oxidized to nickel oxide in the temperature range of 220–480°, neither by air nor by oxygen (dry or moist). Moissan, on the contrary, thought that nickel sub-oxide was oxidized easily at 350–440° to give various products, the composition of which depended upon the temperature of oxidation.

All my experiments on the oxidation and reduction of nickel led me to the conclusion that previous opinions concerning the nature of the oxides of nickel must be modified considerably and abandoned in some cases. At the present time I am greatly interested in the questions concerning the conditions of preparation of pure nickel oxide and of magnetic oxide and also the conditions of conversion (if such conditions exist) into nickel sub-oxide. It is also extremely interesting to study the rôle of water (which is eliminated only with great difficulty from the oxides) which plays an important part in the reactions of reduction and oxidation. Without doubt, it is a true catalyst in these processes. All these questions I propose to study in the future.

Experimental results invariably pointed to the conclusion that there is no oxide of nickel corresponding to the formula Ni_2O_3. This conclusion was later confirmed when I made experiments on the displacement of metals and their oxides from salt solutions by hydrogen under pressure. Experiments with various salts of nickel showed that it was impossible to obtain a crystalline nickel oxide corresponding to the formula Ni_2O_3. An oxide of the formula NiO always separated from the aqueous solutions of nickel salts and was also obtained in crystalline form [2] by displacement from solutions by hydrogen.

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[1] Nickel sub-oxide serving for these experiments contained traces of reduced nickel.

[2] Ipatieff and Kondarev, Ber., *59*, 1421 (1926).

The case of cobalt oxide is entirely different. By the action of hydrogen under pressure upon the salts of cobalt, a crystalline cobalt oxide was separated which corresponded to the formula Co_2O_3.[1] Likewise, crystalline oxides corresponding to Fe_2O_3 and $Fe_2O_3 \cdot FeO$ were obtained by the action of hydrogen upon salts of iron. The commercial black and brown nickel oxides represent mixtures of nickel oxides, most probably, a mixture of nickel suboxide (NiO) with some higher oxide of nickel, such as NiO_2 or others, formed by oxidation during precipitation by chlorine or bromine.

REDUCTION OF NICKEL OXIDES UNDER HIGH PRESSURE

The procedure in this case was to place a weighed amount of nickel oxide in a glass tube in the high pressure apparatus, to pump in a definite pressure of hydrogen, and to heat for a certain length of time at a certain temperature. Sometimes, a copper tube was substituted for the glass tube but the results were the same. The data are presented in Table 57.

The nickel oxide used in the reduction experiments under high pressure contained 72.36% of nickel. When it was heated at 170–180° in a glass tube in the high pressure apparatus, in the absence of hydrogen, the nickel content rose to 73–74%, due to loss of water. When heated at 172° with hydrogen (Expts. 1 and 2), the nickel content increased slightly, to 74.5%. The product of reduction was a greenish material which darkened on exposure to air and liberated traces of oxides of nitrogen when treated with nitric acid. It was evident that only a small amount of reduction took place under these conditions. Starting from 180°, the reduction reaction proceeded more readily and the product contained considerable metallic nickel; reduction to metal at 210° was almost quantitative. In general, it may be said that the reduction proceeds more readily under superatmospheric pressure than at ordinary pressure, temperatures being equal.

Reduced nickel (Expt. 7) was unable to absorb significant amounts of hydrogen, but when exposed to the air it became hot and some of the particles glowed. However, analysis failed to detect any appreciable oxidation of the nickel.

Nickel sub-oxide had an entirely different behavior toward high pressure reduction. At 172° (Expts. 8, 12) it was reduced to

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[1] Ipatieff and Zvyagen, Ber., *44*, 1712 (1912).

TABLE 57

Expt. No.	Nickel Oxide	Amt. of Oxide, G.	Tube	Initial Pressure, Atms.	Maximum Press., Atms.	Final Press., Atms.	T., ° C.	Time, Hrs.	% Ni	Formation of Nitrogen Oxides
1	Ni_2O_3	2.5	Glass	102	142	100	172	11	74.40	Traces
2	Ni_2O_3 Dried at 225°	2.5	"	103	142	102	172	12	74.56	"
3	Ni_2O_3	2.5	"	98	132	97	175	12	76.21	"
4	"	2.5	"	94	129	97	180	12	85.16	Considerable
5	"	11.0	Copper	100	140	90	202	28	89.48	Violent
6	"	5.0	"	82	100	68	210	22	96.44	"
7	Reduced Ni	2.0	Glass	100	147	100	200	5	95.22	"
8	NiO	2.5	"	100	135	95	172	12	95.62	"
9	Ignited NiO	2.5	"	90	129	88	172	14	78.68	None
10	Ignited NiO	2.5	"	90	137	90	172	12	78.26	"
11	Ignited NiO	2.5	"	93	143	90	250	10	80.46	Traces
12	NiO	2.0	"	112	161		172	12	94.4	Violent
13	"	11.0	Copper	88	103	70	200	12	96.6	"
14	Ni_2O_3	3.0	" 39% O_2; 59% N_2	98	212		450	3	76.04	None
15	NiO	5.0	Copper 50% N_2; 50% O_2	100	221		450	6	78.24	"

metallic nickel whereas at ordinary pressure this reduction occurred only above 200°. However, when nickel sub-oxide was ignited in a crucible, it lost completely its capacity for reduction at 172°, and even at 250° (Expt. 11) there was only slight reduction to metallic nickel. Here, as in the oxidation reaction, we see the importance of water. In the present case, it also plays the part of a catalyst.

By heating nickel oxides with air enriched with oxygen in the high pressure apparatus (Expts. 14 and 15) at 415°, no transition of nickel sub-oxide into nickel oxide was observed in spite of the high pressure.

To determine the catalytic ability of nickel oxide to promote the combination of hydrogen and oxygen to form water, the following experiments were made.

Nickel oxide, as shown by the experiments, is a catalyst for the combination of oxygen and hydrogen to form water. In spite of the fact that the gases were diluted with nitrogen and an excess of hydrogen, a spontaneous combination of hydrogen and oxygen took

TABLE 58

Expt. No.	Oxide	Amt. of Oxide, G.	Composition of Gas	Starting Pressure, Atms.	P_{max}, Atms.	Final Pressure, Atms.	T., ° C.	Time		% of Nickel	Formation of Nitrogen Oxides
								Hrs.	Min.		
1	Ni_2O_3 Brownish	2.0	50 Atms. H_2 35 Atms. air	85		62	170	17	00	93.98	Violent
2	Ni_2O_3 Chemically Pure	2.5	50 Atms. H_2 50 Atms. air	100	128	76	168	2	10	77.98	Moderate
3	Ni_2O_3 Brownish	2.0	49 Atms. H_2 51 Atms. air	101		60	751	0	50	80.6	Moderate

place at 160–170°. In one experiment there was an explosion, the arrow of the pressure gage at once falling to 30–40 atmospheres and then rapidly dropping considerably lower than the maximum pressure which preceded the explosion. When the apparatus was cooled rapidly and the gas and nickel oxide analyzed, it was found that the gas did not contain any oxygen and that the nickel oxide was partially reduced.

A careful review of the data obtained leads me to present a certain question which I deem of sufficient importance to mention since its answer is necessary in order to find an explanation of the action of nickel oxide as a catalyst in reduction and oxidation reactions. The above experiment showed that the reduction of nickel oxide proceeds more readily in the presence of a mixture of hydrogen and oxygen than with hydrogen alone, at the same temperature. Inasmuch as the combination of hydrogen and oxygen in the presence of nickel occurs at temperatures around 160°, at which temperature nickel oxide is scarcely reduced at all by hydrogen alone, either we have to assume that the reduction of nickel oxide is catalyzed by the formation of water, or we have to assume that the ability of nickel oxide to be reduced to the metallic state is increased by the presence of oxygen and that metallic nickel serves as a catalyst in the oxidation of hydrogen by oxygen.

Reduction of Nickel Oxides during Catalytic Hydrogenation

After the reduction and oxidation reactions of nickel oxides and of reduced nickel had been investigated, experiments were made upon catalytic hydrogenation in the presence of nickel oxides in order to determine what changes take place in the nickel oxides in the presence of substances undergoing hydrogenation.

In the first series of experiments the substances studied were the oxides and sub-oxides of nickel which had been used in the hydrogenation of benzene and naphthol. The commercial nickel oxide used for the hydrogenation contained 0.8% of moisture and 70.18% of nickel, 71% corresponding to the formula Ni_2O_3. The black nickel oxide used once for hydrogenation contained 76.75–76.62% of nickel and 0.38% of carbon. Nickel oxide used three times for hydrogenation contained 82.37% of nickel and 7.45% of iron.[1] The nickel oxide used for the hydrogenation of alpha- and beta-naphthol contained 80.12% of nickel.

Green nickel sub-oxide obtained from Kahlbaum contained 74.66% of nickel before hydrogenation. After hydrogenation of benzene under pressure at 175°, the nickel sub-oxide contained 86.48% of nickel. These preliminary experiments showed that in hydrogenation under pressure nickel oxides suffer very little reduction. In order to investigate more completely the change in nickel oxide on hydrogenation under pressure, a whole series of experiments was made, the data from which are presented in Table 59, on the facing page.

As seen from this data, the hydrogenation of benzene proceeds in the presence of nickel oxide, starting at 172° (Expts. 6, 7, 10) but going slowly at this temperature. During hydrogenation, the nickel oxide experiences but little reduction as shown by the slight liberation of nitrogen oxides when the used catalyst was treated with nitric acid. Even when the hydrogenation of benzene was made at 250° and the nickel oxide was placed in the tube above the benzene (Expts. 1, 8, 9), reduction occurred only to a slight extent. On the other hand, the reduction of nickel oxide under high pressure by hydrogen in the absence of hydrogenating substance proceeds almost to the end at 200°. Extensive reduction of nickel oxide may occur, however, in the presence of benzene, if

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[1] This iron came from the walls of the bomb.

TABLE 59

EXPT. No.	CATALYST	SUBSTANCE	TUBE	PRESS., INITIAL ATMS.	PRESS., MAX. ATMS.	PRESS., MIN. ATMS.	T., °C.	TIME, HRS.	% Ni	PRODUCT
1	Ni_2O_3	Benzene	Iron				250		76.75	Pure C_6H_{12}
2	Ni_2O_3 Used Three Times	Benzene Ni_2O_3 over benzene	Iron				250		82.37	Pure C_6H_{12}
3	Ni_2O_3	Benzene over Ni_2O_3	Glass				200		93.2	Pure C_6H_{12}
4	"	Beta-naphthol	Iron				240	50	80.12	Hexahydro-beta-naphthol
5	"	Benzene	Copper	100	142	38	201	19	77.85	Pure C_6H_{12}
6	"	Benzene	Copper	105	150	58	172	22	74.4	50% C_6H_{12}, 50% C_6H_6
7	Ni_2O_3 Brownish	Benzene	Iron	110	158	31	174	10	74.66	Pure C_6H_{12}
8	Ni_2O_3 Brownish	Benzene Ni_2O_3 over benzene	Iron	100	160	29	260	1.5	79.00	Pure C_6H_{12}
9	Ni_2O_3 Brownish	Benzene Ni_2O_3 over benzene	Iron				250	2	77.74	Pure C_6H_{12}
10	Ni_2O_3	Benzene Ni_2O_3 over benzene	Iron	110	142	55	173	12	73.87	C_6H_{12}, C_6H_{12}, and C_6H_6
11	NiO	Benzene NiO over benzene	Copper	112	161	85	172	29	94.4	C_6H_{12} and C_6H_6
12	NiO Ignited	Benzene NiO over benzene	Copper	120	173	118	173	29	78.8	C_6H_6
13	NiO Ignited	Benzene NiO over benzene	Iron	110	172	30	215	23	80.64	Pure C_6H_{12}
14	NiO Ignited	Benzene NiO over benzene	Iron	119	180	39	250	22	81.64	Pure C_6H_{12}

the experiment is carried out under special conditions (Expt. 3). A glass tube containing 20 g. of benzene and 2–2.5 g. of nickel oxide was placed in the apparatus and hydrogen pumped in. At the end of the reaction, which took place at 200°, a dry powder was present in the glass tube which consisted of almost pure nickel, the benzene having been converted into pure hexahydrobenzene. Thus, the wetting of nickel oxide by benzene or hexahydrobenzene prevents the reduction of nickel oxide to the metallic state.

It was learned that nickel sub-oxide could also be reduced at 172° to metallic nickel in the presence of benzene (Expt. 11) as well as in the absence of benzene. But, if the nickel sub-oxide was first ignited and afterwards used as catalyst (Expt. 12), it was found to have lost its ability to hydrogenate benzene at 173° and also to be reduced at this temperature by hydrogen alone.

Only when the temperature was raised above 200° (Expts. 13 and 14) did it recover its ability to hydrogenate benzene and in this reaction it was reduced to a very slight extent. This experiment indicates the great significance of water in hydrogenation reactions.

Experiments on the reduction of nickel oxides by hydrogen and also their behavior in hydrogenation catalysis convinced me that my hypothesis concerning the catalytic action of metals and oxides upon alcohols and polymethylene hydrocarbons was correct and induced me to apply it in the hydrogenation of aromatic hydrocarbons. As in the aldehyde decomposition of alcohols, an essential significance is ascribed to water which is decomposed by the metal to give hydrogen *in statu nascendi*, and metal oxide which oxidizes the alcohol; likewise, in hydrogenation catalysis, experiments lead one to the conclusion that water plays the same rôle.

In applying this hypothesis to hydrogenation catalysis, the question as to what is the actual catalyst in hydrogenation, reduced nickel or its oxides, will be discussed first. If no trace of metallic nickel were formed in hydrogenation, starting with nickel oxides, it would be obvious that the catalyst was nickel oxide. And if the conclusions of Moissan concerning the reduction of nickel oxides were correct, they would constitute excellent evidence that only the oxides are catalysts in reduction catalysis. But, my experiments indicated that the reduction of the oxides of nickel proceeds in a manner different from that pictured by Moissan and that in hydrogenation reactions there is always formation of metallic nickel (in traces, it is true). Thus, the answer to this question becomes complicated. In order to answer it, I tried to compare the maximum velocity of hydrogenation of benzene at 250° in the presence of nickel oxide and at 270–280° in the presence of reduced nickel under as nearly identical conditions as possible. The value of $(dP/dt)_{\max}$ for nickel oxide in all the experiments was considerably greater than the same value for reduced nickel and this comparison indicated that the metal oxide plays an essential part in hydrogenation catalysis.

If, in the presence of reduced nickel the maximum velocity of the reaction had been greater, then the hypothesis of the formation of metal hydride would have been more tenable, but in the face of experimental data this hypothesis is greatly weakened. As evidence for the opinion that nickel oxide promotes catalytic action the fact should be mentioned that in spite of the high temperature (250–260°) the percentage of nickel increases but slightly, e.g., from 74% (in the original oxide) to 77%. Comparing the maximum velocity of the hydrogenation of benzene by slightly ignited nickel sub-oxide containing about 2% of water with the velocity of hydrogenation by nickel oxide, we found that the former reaction proceeds more slowly than the latter but more rapidly than in the case of reduced nickel. Consequently, nickel oxides promote more intensive hydrogenation than reduced nickel. If, after mentioning these facts of hydrogenation catalysis, we will recall the hypothesis which I proposed to explain the catalytic dehydrogenation of alcohols, many of the phenomena observed in hydrogenation in the presence of nickel oxides and reduced nickel will become readily understandable.

In the presence of reduced nickel (which always contains nickel oxides and moisture), hydrogen under pressure and at a suitable temperature will reduce the oxide to metal with the formation of water. If at the same time an organic substance is present, the final result is decomposition of the water with resultant formation of nickel oxide and hydrogenation of the organic compound. As evidence, it may be stated that under these conditions nickel does not absorb hydrogen, even under pressure, to form metal hydride. Besides this, when reduced nickel is exposed to the air after heating under high pressure with hydrogen at 200°, it heats up considerably, which fact indicates that the nickel is in a highly active state. When reduced nickel is heated at 280–290° with hydrogen at ordinary pressure it does not heat upon exposure to the air. If this explanation of catalysis by reduced nickel is correct, then nickel oxide should develop a greater maximum velocity at the beginning of the reaction than reduced nickel since at the beginning of the reaction more water will be available in the former case for the liberation of hydrogen. Nickel oxide ought to give a maximum velocity of hydrogenation because it is an oxide rich in oxygen. It may be possible that the reduction of nickel oxides by hydrogen does not proceed to the formation of metallic nickel but only to the formation of lower oxides which function in the same way as reduced nickel.

That water plays an essential part in hydrogenation catalysis has been shown by many experiments. In regard to nickel oxide, it should be noted that it retains water with unusual tenacity and that it is necessary to heat the oxide above 300° in order to remove water completely. Dried nickel oxide absorbs moisture readily, and it is possible that the hydrates of nickel oxide are of importance in the reduction and oxidation reactions of nickel oxide.

HYDROGENATION OF HYDROCARBONS

NICKEL OXIDE CATALYST; APPARATUS FOR HYDROGENATION[1]

Experiments on the catalytic hydrogenation of organic compounds were first made in my ordinary high pressure apparatus without stirring. However, the necessity of thoroughly mixing the material undergoing hydrogenation and the catalyst was soon apparent; the speed of hydrogenation was greater and the material suffered less decomposition when the mixture was stirred. Several methods of agitation were tried. In 1909, a stirrer made by my assistant Werhowsky was used. The action of this stirrer was based on the principle of a solenoid. By connecting and disconnecting the current, a shaft attached to a perforated stirrer was made to rise and fall, thus agitating the mixture in the high pressure apparatus. Its principle advantage was the possibility of stirring under very high pressures since there was no danger of leakage through a packing gland. This stirrer was first applied in the stirring of solutions of copper sulphate in experiments on the displacement of metallic copper by hydrogen and it was later used in the hydrogenation of various unsaturated compounds and monosaccharides.[2]

Another kind of a stirrer for use in hydrogenation was constructed at my suggestion in the machine shop of the Academy of Science by Mr. Masing and also in the Langensippen machine shop in St. Petersburg. The stirrer was given a vertical motion by means of a worm gear and consisted of a shaft to which were attached 7 or 8 circular plates, the diameters of which were slightly less than the diameter of the tube in which they operated. With sixty to seventy churnings per minute, the stirrer mixed the catalyst with the liquid very well and the hydrogenation proceeded with great rapidity. Provided the stem of the stirrer was well fitted in its bearing and the packing gland was carefully filled (with asbestos, graphite, and grease) and water cooled, it was possible to work under pressures of 50 to 70 atmospheres. When necessary, the experiment could be interrupted and additional hydrogen pumped into the bomb. This type of apparatus was employed in most of the hydrogenation experiments on fats, hydrocarbons, and other compounds.

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[1] See p. 32 for description of apparatus.

[2] Ipatieff, Ber., *45*, 3219 (1912).

In the laboratory of the Artillery Academy, special swings were employed for the purpose of agitation. The high pressure apparatus was fastened in a wooden frame which was swung to and fro at any desired speed. The German firm of Andreas Hofer in Germany built the high pressure apparatus and arranged for the mixing of the contents by rotation of the bomb itself, but this apparatus was not suitable because of their method of closing the bomb. Their system of closure necessitated a narrow neck which made cleaning difficult and it was also impossible to place various sizes of tubes in the bomb. At this point, I redesigned the rotating autoclave, substituting my method of closure (a knife edge making contact with a copper gasket) so there was no need of constricting the neck of the bomb. This change made possible the rotation of the apparatus by means of the usual transmission and permitted the construction of a bomb capable of holding 5 liters with a secure closure. At present we are using such an apparatus with straight sides and find it very convenient and cheap, and capable of withstanding a working pressure of 300 atmospheres at temperatures up to 500°.

HYDROGENATION OF ANTHRACENE AND PHENANTHRENE[1]

By the hydrogenation of anthracene at ordinary pressure in the presence of reduced nickel Godchot obtained tetrahydro- and octahydroanthracene. The latter can also be obtained by repeated hydrogenations of tetrahydroanthracene or by the reduction of anthraquinone in the presence of nickel oxide under an initial pressure of 100 atmospheres; further hydrogenation gives perhydroanthracene, $C_{14}H_{24}$,[1] in good yield. Godchot obtained perhydroanthracene from octahydroanthracene by heating the latter with red phosphorus and iodine in a sealed glass tube at 250° or at ordinary pressure, by passing it with hydrogen through a tube containing reduced nickel. As might be expected, Godchot [2] preferred the latter method of obtaining perhydroanthracene. He noted the formation of another substance, a liquid hydrocarbon, which he did not investigate.

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[1] Ipatieff, Jakowlew, and Rakitin, Ber., *41*, 996 (1908).

According to the experiments of Schmidt and Metzger [3] the hydrogenation of phenanthrene at ordinary pressure in the presence of reduced nickel is limited to the addition of two hydrogen atoms, further addition of hydrogen being possible only by reaction with iodine and phosphorus in a sealed tube. They were unable to obtain perhydrophenanthrene and they also showed that Liebermann and Spiegel,[4] who worked with hydrogen iodide and phosphorus, had not obtained the perhydro compound. By applying high pressure of hydrogen in the presence of nickel oxide, Ipatieff and Rakitin succeeded in hydrogenating phenanthrene completely to perhydrophenanthrene ($C_{14}H_{24}$), and together with Jakowlew, I also obtained complete hydrogenation of anthracene to perhydroanthracene.

Hydrogenation of Anthracene.—In order to hydrogenate anthracene completely, it was necessary to subject it to a triple hydrogenation.

In the first hydrogenation, 25 g. of anthracene and 2 g. of nickel oxide under an initial hydrogen pressure of 100–125 atmospheres were heated at 260–270° until there was no further change in pressure, 10–15 hours being required. The solid product of the reaction was extracted from the tube by means of ether. The recrystallized product did not have a constant melting point (88–105°) and, doubtless, consisted of a mixture of several hydrocarbons. However, by means of fractional distillation and recrystallization it was possible to separate a considerable amount of a product melting at 103–105° which according to analysis corresponded fairly well to the formula for tetrahydroanthracene whose structure is probably as follows:

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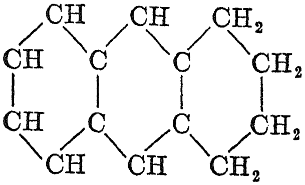
[1] Godchot, Compt. rend., *139*, 605 (1904).

[2] Godchot, Ber., *22*, 779 (1889).

[3] Schmidt and Metzger, Ber., *40*, 4240 (1907).

[4] Liebermann and Spiegel, Ber., *22*, 779 (1889).



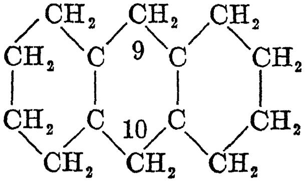
It has one ring of a naphthenic character and is similar to tetrahydronaphthalene.

Anal. Calcd. for $C_{14}H_{14}$: C, 92.3; H, 7.7. Found: C, 92.1; H, 7.6.

In the second hydrogenation, the product of the first hydrogenation was used which consisted chiefly of tetrahydroanthracene. It was carried out under the same conditions but it is to be noted that the reaction was much more energetic. The solid reaction product crystallized nicely from alcohol in the form of plates which physically resembled those of naphthalene, except that they were odorless. The material melted at 73–74°. Analyses of this material obtained from different experiments were all the same.

Anal. Calcd. for $C_{14}H_{20}$: C, 89.4; H, 10.6. Found: C, 89.2; H, 10.5.

As shown by the data, the hydrocarbon obtained by the second hydrogenation of anthracene was *decahydroanthracene,* $C_{14}H_{20}$. Its melting point was two degrees higher than that of the hydrocarbon of Godchot [1] which he obtained by the hydrogenation of anthracene at ordinary pressure and which he considered to be octahydroanthracene. Both hydrocarbons are very similar, but the hydrocarbon which I obtained (m.p., 73–74°) had an analysis corresponding to that of decahydroanthracene.



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[1] Godchot, Compt. rend., *139*, 605 (1904).

Anal. Calcd. for $C_{14}H_{18}$: C, 90.3; H, 9.7. Calcd. for $C_{14}H_{20}$: C, 89.4; H, 10.6. Found: C, 89.1, 89.2; H, 10.4, 10.5.

It has two naphthenic nuclei and probably two atoms of hydrogen are on the gamma carbons (carbons 9 and 10).

Decahydroanthracene had already been obtained by Lucas,[1] but his experimental data are both brief and inaccurate. The analyses by Lucas correspond equally well for dodecahydroanthracene and decahydroanthracene. Since Lucas' hydrocarbon melted at 52–53°, it is safe to assume that he did not have decahydroanthracene.

Anal. (Lucas). Calcd. for $C_{14}H_{20}$: C, 89.4; H, 10.6. Calcd. for $C_{14}H_{22}$: C, 88.4; H, 11.6. Found: C, 88.6; H, 11.0.

For the third hydrogenation, the product of the second hydrogenation (i.e., decahydroanthracene) was used. The reaction conditions were the same and the product of the reaction was a liquid of decided odor from which crystals readily separated. The liquid distilled at 272–277° and gave the following analytical figures.

Anal. Calcd. for $C_{14}H_{24}$: C, 87.5; H, 12.5. Found: C, 87.3; H, 12.6.

According to analysis the liquid hydrocarbon was perhydroanthracene. The yield of hydrocarbon was satisfactory, 18 g. of pure product [2] being obtained from 23 g. of decahydroanthracene. On standing, an abundant yield of crystals separated from the liquid and after crystallization from the alcohol the material melted at 88–89°. The remaining liquid, which did not crystallize at ordinary temperature, solidified in a cooling mixture to a crystalline mass which melted at $-3°$.

The crystalline product melting at 88–89° was pure perhydroanthracene as shown by analysis and also by its total inability to react with bromine or with nitrating mixture.

Anal. Calcd. for $C_{14}H_{24}$: C, 87.5; H, 12.5. Found: C, 87.4, 87.4; H, 12.4, 12.5.

It dissolved readily in alcohol, ether, benzene, and ligroin and crystallized well from the last named. Determination of its molecular weight in the Beckman apparatus gave the value 192 which corresponds to the theoretical. As to whether the liquid product was identical with the crystalline substance, it is impossible to state at the present time. In all probability it was a geometrical isomer.

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[1] Lucas, Ber., *21*, 2510 (1888).

[2] This part of the product remained in the apparatus—on the walls, in the tube of the manometer, etc.

Under the conditions described above, theoretical yields could not be obtained by repeated hydrogenation of anthracene since part of the hydrocarbon decomposed during hydrogenation with liberation of carbon and formation of methane. Analysis of the gas resulting from repeated hydrogenation gave the following figures.

TABLE 60

Hydrogenation No.	Volume of Gas, Liters	Hydrogen, %	Methane, %
1	4.8	83.0	16.1
2	8.0	79.5	21.0
3	16.0	88.0	11.5

The nickel oxide used in these repeated hydrogenations was not reduced to metallic nickel [1] in spite of the high temperature, high pressure, and long heating.

Hydrogenation of Phenanthrene.—This hydrogenation was carried out under the same conditions as those employed in the case of anthracene, only it was necessary to maintain a considerably higher temperature, in some cases up to 400°. However, there was no separation of carbon or formation of methane.

The results of this series of hydrogenations are presented in the following table.

TABLE 61

Substance	T., °C.	Time, Hrs.	Press., Atms.			Products	Boiling Point, °C.	Melting Point, °C.	Picrate, M.P., °C.
			Initial	Max.	Final				
$C_{14}H_{10}$ 25 g.	320	17	100	162	53	Liquid $C_{14}H_{12}$ and $C_{14}H_{14}$	310–318	Solidified in ice	105–106 137–138
$C_{14}H_{12}$ $C_{14}H_{14}$ 25 g.	360	24	100	168	63	Liquid $C_{14}H_{18}$	290–300	Solidified in ice plus salt	
$C_{14}H_{18}$ 20 g.	370	12	100	152	60	Liquid $C_{14}H_{24}$	270–276		

In the first hydrogenation of phenanthrene, a colorless liquid was obtained in theoretical yield which, on exposure to air, became yellow and decolorized potassium permanganate solution.

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[1] Ipatieff, J. Russ. Phys. Chem. Soc., *40*, 1 (1908).

On standing, a solid hydrocarbon settled out, which according to analysis, was a dihydrophenanthrene.

Anal. Calcd. for $C_{14}H_{12}$: C, 93.3; H, 6.7. Found: C, 93.8; H, 6.5.

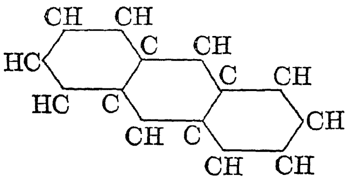
The liquid product of the reaction consisted of a mixture of *tetrahydrophenanthrene* and *dihydrophenanthrene* as evidenced by the formation of two picrates, melting at 105–106° and 135–137°, respectively. The picrate melting at 105–106°, orange-red needles, corresponded to tetrahydrophenanthrene.

Anal. Calcd. for $C_{14}H_{14}C_6H_3N_3O_7$: N, 10.2. Found: N, 10.5.

The second hydrogenation gave a liquid which solidified in a mixture of snow and salt to a crystalline mass melting at −4 to −5°. It was slightly soluble in alcohol, dissolved easily in ether and benzene, and upon standing acquired a yellow coloration. Nitrating mixture acted energetically with it. According to analysis, its composition corresponded to octahydrophenanthrene, $C_{14}H_{18}$. The yield of hydrocarbon was quantitative.

Anal. Calcd. for $C_{14}H_{18}$: C, 90.3; H, 9.7. Found: C, 90.1, 90.2; H, 9.7, 9.7.

We may safely assume that the first hydrogenation of phenanthrene gave chiefly tetrahydrophenanthrene by the addition of four atoms of hydrogen to one of the benzene rings, thus forming a naphthenic ring similar to that in tetrahydronaphthalene. Further hydrogenation added four more hydrogen atoms to form octahydrophenanthrene, a hydrocarbon with two naphthenic rings.



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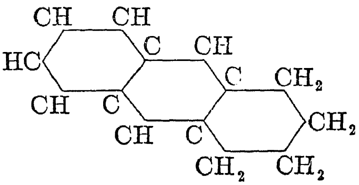

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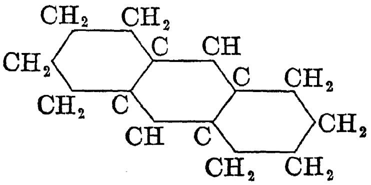

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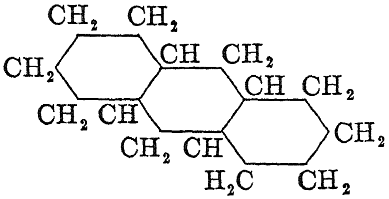

The third hydrogenation gave the final product, perhydrophenanthrene ($C_{14}H_{24}$) by addition of six more atoms of hydrogen. It was a colorless liquid with an odor reminiscent of rubber. It did not solidify in ice or in a mixture of ice and salt; on long standing in the light, it acquired a slightly yellowish color. It was not acted upon by bromine, potassium permanganate, or nitrating mixture. In spite of the fact that the product distilled at a high temperature (266–276°) the analytical figures showed that it was quite pure. Analyses showed that both fractions ([1] b.p., 266–270° and [2] b.p., 270–276°) were identical in composition, corresponding to that of perhydrophenanthrene (different isomers).

Anal. Calcd. for $C_{14}H_{24}$: C, 87.5; H, 12.5. Found: Fraction (1) C, 87.6; H, 12.6; Fraction (2) C, 87.7; H, 12.2.

Thus, by means of hydrogen under pressure and a nickel oxide catalyst it is easy to obtain the various hydrogenation products of phenanthrene up to perhydrophenanthrene. In spite of the high temperature the yield of the product is almost quantitative, the phenanthrene molecule being more stable than that of anthracene. The residual gas from the hydrogenation consists almost wholly of pure hydrogen. Previously, no one had succeeded in obtaining perhydrophenanthrene, $C_{14}H_{24}$.

Concerning the hydrogenation of phenanthrene with other catalysts and the identification of the intermediate products of hydrogenation, more will be said in the chapter on destructive hydrogenation.

Hydrogenation of Fluorene, Acenaphthene, and Retene [1]

After the experiments on the hydrogenation of naphthalene, anthracene, and phenanthrene had shown the possibility of complete hydrogenation in the presence of nickel oxide under pressure, a study of the conditions for hydrogenating other polynuclear aromatic hydrocarbons was initiated. Up to this time, by hydrogenation at ordinary pressure in the presence of reduced nickel according to the method of Sabatier, it had not been possible to obtain complete hydrogenation, and the usual method of hydrogenation, with hydrogen iodide and phosphorus in sealed tubes, did not always give the desired results. For example, by the latter method the hydrogenation of phenanthrene does not go to completion and perhydrophenanthrene is not formed, as shown by the experiments of Schmidt and Metzger,[1] as well as those of Ipatieff and Rakitin.[2] Likewise, the hydrogenation of fluorene does not proceed to completion as shown by Schmidt and Fischer [3] and, if under certain conditions perhydrofluorene is obtained, it is contaminated by the lower products of hydrogenation.

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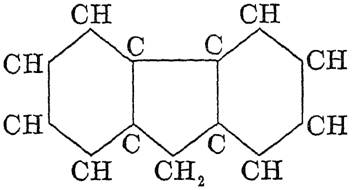
[1] Ipatieff, Ber., *42*, 2092 (1909).

Fluorene.—



The hydrogenation of fluorene was carried out in the high pressure apparatus, starting with 20 g. of fluorene, 3 g. of nickel oxide, and 120 atmospheres of hydrogen, the temperature being below 290°. The reaction proceeded rapidly and after 24 hours, perhaps sooner, it was complete as shown by the constant pressure within the apparatus. The hydrocarbon product distilled at 255–265°, reacted with nitrating mixture, and slightly with potassium permanganate solution. According to the analysis, the product was *decahydrofluorene* ($C_{13}H_{20}$).

Anal. Calcd. for $C_{13}H_{20}$: C, 88.6; H, 11.4. Found: C, 88.7; H, 11.4.

According to later experiments (see chapter on destructive hydrogenation), as well as those on the hydrogenation of naphthalene and phenanthrene, we can readily explain the addition of eight atoms of hydrogen to two benzene rings with the formation of *octahydrofluorene* with two naphthenic rings.

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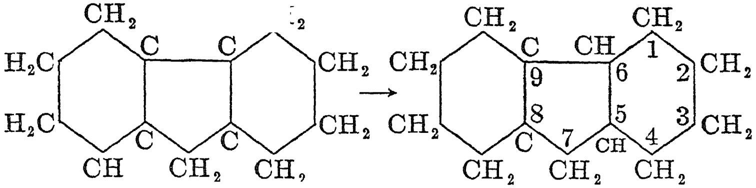
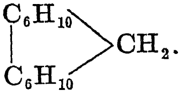
[1] Schmidt and Metzger, Ber., *40*, 1289 (1907).
[2] Ipatieff and Rakitin, Ber., *41*, 997 (1907).
[3] Schmidt and Fischer, Ber., *41*, 4227 (1908).



But to explain the addition of two more hydrogen atoms with the formation of decahydrofluorene presents certain difficulties. It is necessary to assume that the hydrogen adds only to the carbons in the 5 and 6 positions and in order to obtain perhydrofluorene (by the addition of two more hydrogens) further hydrogenation is necessary. At the present time, it is difficult to assign a structure to the decahydro derivative, the initial product of hydrogenation.

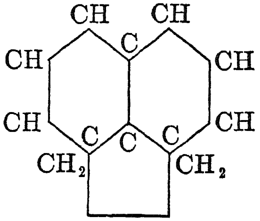
The decahydrofluorene was subjected to a second hydrogenation under a high pressure of hydrogen in the presence of nickel oxide at 285°. The reaction was considered finished when the pressure in the apparatus became constant, which happened within eight hours. The hydrocarbon product distilled chiefly at 254–258°, a very small portion distilling at 258–262°. The yield was almost quantitative and the gas remaining in the apparatus was hydrogen. The hydrogenated fluorene did not react at once with nitrating mixture but after standing for a certain length of time a reaction set in which was probably due to the unstable ring closure and not to the nitration of the hydrocarbon itself. An alcoholic solution of potassium permanganate was not decolorized. The specific gravity of the hydrocarbon was: d_0, 0.950. Analysis showed that both liquid fractions had the same composition. According to analysis and properties, the hydrocarbon product was a perhydrofluorene,



$\begin{matrix}C_6H_{10}\\ | \\ C_6H_{10}\end{matrix}\!\!>\!CH_2$. It is readily obtainable by this method.

Anal. Calcd. for $C_{13}H_{22}$: C, 87.6; H, 12.4. Found (b.p., 254–258°): C, 87.6, 87.7; H, 12.8, 12.6. Found (b.p., 258–262°): C, 88.1; H, 13.4.

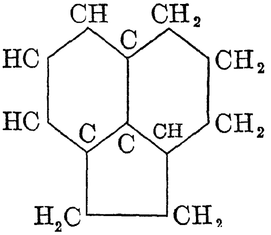
Acenaphthene.—Hydrogenation of acenaphthene was performed under the same conditions as those described for fluorene. The temperature was maintained at 290–300° and the duration of the experiment was 24 hours. The final product of hydrogenation was not usually formed in the first hydrogenation but rather a mixture of more or less hydrogenated hydrocarbons. However, in certain cases, decahydroacenaphthene could be obtained in the first hydrogenation.



The first hydrogenation product of acenaphthene boiled at 245–255° and reacted vigorously with nitrating mixture, showing the presence of aromatic nuclei. As shown by the analysis, the product was closely related to *tetrahydroacenaphthene.* Thus, we have here the same hydrogenation steps as observed in the hydrogenation of naphthalene and of beta-naphthenic acid.

Anal. Calcd. for $C_{12}H_{12}$: C, 91.1; H, 8.9. Found: C, 90.8; H, 9.6.

Therefore, the structural formula should be:

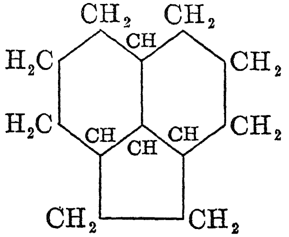


In order to obtain complete hydrogenation, the primary product was subjected to the further action of hydrogen under pressure at 290–300° in the presence of nickel oxide, the reaction requiring only a short time. The product boiled mainly at 230–234°, only a small part distilling at 234–240°. Neither of these fractions decolorized potassium permanganate solution or reacted with nitrating mixture. The specific gravity of the hydrocarbon was d_0, 0.938.

Analysis of the two fractions gave the following results:

Anal. Calcd. for $C_{12}H_{20}$: C, 87.8; H, 12.2. Found: (1) C, 87.8; H, 12.3; (2) C, 87.8; H, 12.5.

The analytical figures and the chemical properties permit the assumption that the product (both fractions) of the second hydrogenation of acenaphthene was decahydroacenaphthene.

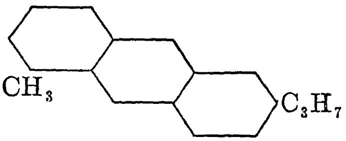


In this case, and also in the case of the hydrogenation of naphthalene, phenanthrene, etc., it was observed that the product of complete hydrogenation boiled over a temperature range and, therefore, we must assume that isomerization took place simultaneously with hydrogenation.

Hydrogenation of Retene

It was suggested to me by Professor Bamberger that I study more closely the hydrogenation of retene as he was desirous of obtaining the product resulting from the complete hydrogenation of this compound, presumably $C_{18}H_{32}$, which up to this time was unknown. Bamberger[1] thought that completely hydrogenated retene might be similar to a hydrocarbon called Fichtelite which is found, together with retene, in peat bogs in Bavaria, Germany.

Retene is 1-methyl-4-isopropylphenthrene:



Its structure had been determined by Bamberger and Hooker[2] by means of hydrogenation (according to the old hydrogen iodide-phosphorus method). Liebermann and Spiegel[3] had obtained dodecahydroretene ($C_{18}H_{30}$) as the most highly hydrogenated product of retene. Natural Fichtelite, when heated with iodine, loses two hydrogen atoms and forms dodecahydroretene which indicates the possibility that synthetic Fichtelite might be formed by the complete hydrogenation of retene. But my experiments did not confirm this belief.

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[1] Bamberger, Ber., *22*, 635, 3361 (1889).

[2] Bamberger and Hooker, Ann., *229*, 102 (1885).

[3] Liebermann and Spiegel, Ber., *22*, 730 (1889).

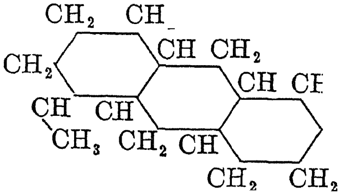
For the hydrogenation experiments, I used retene received from Bamberger and also from Kahlbaum. The reaction was performed in the high pressure apparatus in the presence of nickel oxide catalyst at 350–360° and 120 atmospheres initial pressure of hydrogen. The first hydrogenation of retene proceeded rapidly and not to completion; the product obtained distilled at 339–340° and reacted vigorously with nitrating mixture. Analysis showed that this product was dodecahydroretene, $C_{18}H_{30}$.

Anal. Calcd. for $C_{10}H_{30}$: C, 87.9; H, 12.2. Found: C, 88.6; H, 11.8.

When the product of the first hydrogenation was again subjected to hydrogenation under the same conditions, a hydrocarbon was obtained which distilled at 300–315° and which did not react with potassium permanganate solution or with nitrating mixture. The analytical figures were close to those of perhydroretene, $C_{18}H_{32}$.

Anal. Calcd. for $C_{18}H_{32}$: C, 87.1; H, 12.9. Found: C, 87.5; 87.5; H, 13.0; 12.7.

Since perhydroretene is a liquid boiling at 300–315°, and not solidifying in a cooling mixture of salt and ice, and Fichtelite is a solid hydrocarbon melting at 46° and boiling at 355°, it is clear that these two hydrocarbons are isomers and distinguished from each other by a difference in the location of the side chains. Therefore, the question regarding the structure of Fichtelite remains open, the structure of perhydroretene being considered to be the following:

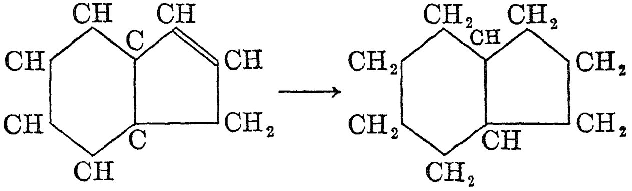


In dodecahydroretene there are three naphthenic rings, but perhaps the middle one is unsaturated inasmuch as the hydrocarbon reacts energetically with nitrating mixture.

HYDROGENATION OF INDENE

In their paper on "Equilibrium in Hydrogenation," Padoa and Fabris[1] showed that indene, when hydrogenated at 300°, according to the method of Sabatier and Senderens, was unable to add hydrogen in the presence of reduced nickel at ordinary pressure. But when the hydrogenation was made at 250°, two atoms of hydrogen were added with the formation of hydrindine which was usually contaminated with small amounts of condensation products. Hydrindine decomposes at 300° into hydrogen and indene.

When indene was hydrogenated in the Ipatieff high pressure apparatus[2] in the presence of nickel oxide, octahydroindene was obtained in excellent yield.



Twenty grams of indene (b.p., 178–179°) heated for 26 hours at 250–260° in the presence of 2 g. of nickel oxide under 110 atmospheres initial pressure of hydrogen yielded a liquid which distilled mainly (16 g.) at 160–168°. The oil remaining after distillation solidified. The liquid hydrocarbon did not decolorize potassium permanganate solution, combine with bromine, or react with nitrating mixture. Redistillation yielded a product boiling at 165–166° at 767 mm.; d_{20}, 0.833. It was a transparent liquid which did not become colored on long heating.

Anal. Calcd. for C_9H_{16}: C, 87.1; H, 12.9. Found: C, 87.1; H, 12.7.

HYDROGENATION OF CARBON; SYNTHESIS OF METHANE[3]

In view of the easy hydrogenation of various organic compounds under pressure, it was most interesting to carry out experiments on the hydrogenation of pure carbon, e.g., to synthesize methane from hydrogen and carbon at the lowest possible temperature. The direct combination of hydrogen and carbon without a catalyst takes place, according to Bone and Jerdan,[1] at a temperature of 1200°. Some acetylene is formed under these conditions and a 1% yield of methane. This result was confirmed later by Bone and Coward [2] who succeeded in obtaining a 75% yield of methane from pure carbon. On the basis of thermodynamic calculations and quantitative experiments, Mayer and Altmayer [3] showed that such a yield of methane was impossible under these conditions. At 800°, 95.5% of hydrogen and 4.4% of methane might be present in a mixture and at lower temperatures a larger quantity of methane must be present. Thus, at 500° the content of hydrogen should be 37.47% and that of methane, 62.53%. This synthesis of methane took place very slowly since there was no catalyst. In order to obtain an equilibrium in the synthesis and decomposition of methane, Mayer and Altmayer conducted a series of experiments in the presence of catalysts, namely, reduced nickel and reduced cobalt. By means of these catalysts, Mayer and Altmayer succeeded in producing the synthesis of methane from carbon and hydrogen in better yields and at comparatively low temperatures. At present, no criticism of the conditions under which these scientists conducted their investigations, nor of their results, will be offered since the experimental data presented is insufficient, but because the question is important, it is not without interest to describe my experiments on the synthesis of methane which were carried out under the influence of various catalysts.

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[1] Padoa and Fabris, Atti. accad. Lincei, [5], *17*, 111 (1908).

[2] Ipatieff, J. Russ. Phys. Chem. Soc., *45*, 994 (1913); C.A., *7*, 1170 (1913).

[3] Ipatieff, J. prakt. Chem., *87*, 479 (1912).

The majority of my experiments on the synthesis and decomposition of methane were made under high pressure and at temperatures not above 520°, although some were performed at ordinary pressure and at 460–650°. In order to explain the catalytic process of the synthesis of methane, it first seemed advisable to make certain experiments on the reduction of carbon dioxide in the presence of various catalysts. Mayer and Altmayer assumed that the synthesis of methane in the presence of reduced nickel was facilitated by the formation of nickel-hydrogen compounds, but I explain the catalysis by the action of metal oxides which function through oxidation and reduction. In the present case, the mechanism is as follows:

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[1] Bone and Jerdan, Chem. News, *74*, 268 (1896).

[2] Bone and Coward, Chem. Soc., *93*, 1975 (1908).

[3] Mayer and Altmayer, Ber., *40*, 2134 (1907).

H. .NiO catalyst
H. . C acceptor

The metal oxide oxidizes the carbon (acceptor) into carbon dioxide which is then reduced to methane.

$$CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O$$

The metal decomposes water and is oxidized thereby, hydrogen is liberated, etc.; thus, a small amount of metal oxide is able to promote the synthesis of a large amount of methane.

Such an explanation of the catalytic synthesis of methane modifies our conception of synthesis as the result of the direct combination of elements to form a complex molecule. One might ask such questions as the following: "Does direct combination of hydrogen and carbon into methane take place at 1200°," as indicated by the experiments of Bone and Jerdan? "Does water participate in the reaction?" "Does the formation of oxides of carbon precede the synthesis of methane?" In order for the latter reaction to occur, only a very small amount of water is required as is necessary in many chemical reactions. The reduction of carbon dioxide by hydrogen under high pressure is *a reversible reaction*[1] since *methane decomposes with separation of hydrogen in the presence of the reduced metal and water.* Water is an oxidizing agent under pressure and at comparatively low temperatures any of my experiments on the displacement of metals show that certain metals, e.g., iron, cannot be obtained from aqueous solution because the metal displaced by the hydrogen is oxidized by the water to the oxide.

Carbon obtained from sugar, and containing about 99% of carbon, and hydrogen prepared from pure zinc and sulphuric acid served for the synthesis of methane. The hydrogen was purified by means of potassium hydroxide, potassium permanganate, copper sulphate, sulphuric acid, palladium chloride, and copper chloride.

The synthesis and decomposition of methane at ordinary pressure were performed in two ways. In the first series of experiments dry hydrogen was passed through a long tube containing a mixture of carbon and nickel oxide (also some reduced nickel). The tube temperature was held at 600–625° and the experiment continued for three hours. Analysis of the gas showed that methane was not present.

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[1] Ipatieff, J. prakt. Chem., *87*, 480 (1912). See "Les Combustibles Liquids . ficiels" by Mailhe, p. 12.

In the second series of experiments, a mixture of 1 g. of reduced nickel and 1 g. of carbon from sugar was placed in a small tube which was fitted into another tube; a pyrometer was in contact with the carbon and the catalyst. The tube was placed in a gas oven, and air was expelled from this tube by pure dry methane. The tube was then heated to chosen temperatures, and samples of the gas were withdrawn and analyzed from time to time. In spite of the fact that the temperature was raised to 600°, a decomposition of methane was observed. Carbon was deposited on the nickel surface and the exit gas contained about 3% of hydrogen. The amount of carbon separated on the surface of the nickel was determined by analysis; 0.6228 g. of catalyst gave 0.050 g. of CO_2 and 0.0007 g. of H_2O which corresponds to 0.02% of carbon.

Under high pressure and at 510–520° in the presence of reduced nickel, the synthesis of methane from carbon and hydrogen took place. For an explanation of the synthesis of methane according to the scheme portrayed above, it was necessary to show that the amount of methane obtained was greater than that corresponding to the carbon dioxide present (formed by the oxidation of carbon by the oxygen of the nickel oxide and by the oxygen in the gas). Methane from this source would not be due to catalytic synthesis but rather to the oxidation of carbon into carbon dioxide followed by the catalytic reduction of the latter. This source of error was eliminated and it was shown conclusively that a catalytic synthesis of methane actually took place in the presence of a number of metallic oxides. Some of the data are presented in the following table.

TABLE 62

Substances	Catalyst	Amount of Catalyst, G.	Starting Press., Atms.	T., ° C.	Time, Hrs.	Methane, %
Carbon Hydrogen	NiO	3	116	520	15	4.9
	NiO	3	110	510	26	6.5
	NiO	1	110	525	20	1.5
	CuO	3	100	510	15	3.4
	SnO	3	102	515	12	6.2
	Fe_2O_3	3	100	520	17	5.0
	Fe_2O_3	3	100	515	16	5.2

A mixture of 3 g. of carbon (from sugar) and 3 g. of metal oxide was placed in the apparatus, hydrogen was pumped in, and the temperature held at 510–520°. It is interesting to note that diffusion of gas through the walls of the apparatus was considerable at this temperature as evidenced by a continuous drop in pressure. From Table 62, it is seen that in the presence of various metal oxides at 510–520° the formation of methane took place (below 500°, no formation of methane occurred); and when a smaller amount of metal oxide was used, less methane was formed. These experiments did not show the catalytic synthesis of methane because the amount of methane could be explained by the reduction of carbon dioxide under the influence of the catalysts, the carbon dioxide resulting from the oxidation of carbon by the oxygen present in the metal oxide.

In order to prove that the catalytic synthesis of methane actually takes place, a series of experiments was made with reduced nickel. The reduced nickel, which could not be reduced further, contained 94.81% of nickel and was therefore assumed to have no oxygen available for the oxidation of carbon. In order to remove all the oxygen from the apparatus the air was pumped out and the apparatus thoroughly rinsed with hydrogen before pumping in fresh hydrogen which was analyzed before the experiment. The catalyst, consisting of 2 g. of reduced nickel and 1 g. of aluminum oxide, was mixed with 1 g. of carbon obtained from sugar. The data are tabulated in the following table.

TABLE 63

REDUCTION OF CARBON IN THE PRESENCE OF REDUCED NICKEL AND ALUMINA

SUBSTANCE, G.	CATALYST	PRESS., ATMS.		T., °C.	TIME, HRS.	ANALYSIS OF HYDROGEN		ANALYSIS OF GAS AFTER EXPT.		
		Start	End			O	H	O	H	CH_4
Carbon and hydrogen	Ni Redu. + Al_2O_3	100	72	468–485	20	0.2	98.8	0.3	98.2	
Carbon and hydrogen	Ni + Al_2O_3	99	65	466–506	19	0.4	98.2	0.3	98.0	
Carbon and hydrogen	Ni + Al_2O_3	82	35	500–509	19	0.4	98.4	0.4	98.0	1.0
Carbon and hydrogen	Ni + Al_2O_3	88	60	500–510	17	0.4	98.4	0.4	98.0	1.2
Carbon and hydrogen	Ni + Al_2O_3	100	54	505–513	21.5	0.4	98.2	0.2	97.8	2.0
Carbon and hydrogen	Ni Redu.	100	56	496–510	18	0.4	98.2	0.5	97.6	1.2
Carbon and hydrogen	Ni Redu. 5 g. H_2O	100	66	496–513	18.5			0.4	98.0	1.2

These experiments showed that at 500° no synthesis of methane took place; at temperatures above 500°, a catalytic synthesis of methane occurred without doubt and the higher the temperature the greater the yield of methane, the limit of the reaction at 500–510° being about 1%. Even with steel tubes and under the conditions previously indicated, it was impossible to work at higher temperatures because the hydrogen diffused through the walls of the apparatus and damaged them considerably.

In order to show that methane decomposed with separation of hydrogen in the presence of reduced metal and water, a series of experiments was made, the results of which are presented in Table 64.

TABLE 64

DECOMPOSITION OF METHANE

SUBSTANCE, G.	CATALYST	PRESS., ATMS.		T., °C.	TIME, HRS.	ANALYSIS OF GAS					
						Before Expt.			After Expt.		
		Start	End			CO_2	O	H	CO_2	O	H
Methane	Ni + 0.5 g. H_2O	30	30	485–520	20	0.4	1.2	1.2	3.0	0.4	5.2
Methane	Ni + 0.5 g. H_2O	39	39	476–510	21	0.8	1.6	0.8	2.5	0.4	3.4
Methane	Ni + 0.5 g. H_2O	24	24	465–510	19		2.6	5.6			8.4
Methane	Ni + 0.5 g. H_2O	29	30	495–522	18	0.4	1.2	1.6	1.2	1.2	3.2
Methane	NiO	22	32	506–518	16	0.4	0.8	2.4	6.0	0.4	2.4
Methane	Zn Dust	27	26	492–502	22	0.5	2.0	2.5	0.4	0.8	2.0

The methane used for the experiments was obtained from sodium acetate and was analyzed before heating. As seen from Table 64, decomposition of methane occurred in the presence of reduced nickel as indicated by the increase of the hydrogen content. At this temperature and in the presence of zinc dust, no decomposition of methane took place.

In order to study the reversibility of the reduction of carbon dioxide by hydrogen, a series of experiments was made at ordinary pressure, as well as at superatmospheric pressure.

At *ordinary pressure*, a definite mixture of carbon dioxide and hydrogen was passed through a thick layer of reduced nickel at 450°. The experiments showed that in the presence of an excess of carbon dioxide (150%) there was almost complete removal of hydrogen by the reduction reaction. When the theoretical amount of hydrogen was taken, a considerable quantity of it remained unreacted, 15–25%.

In the high pressure experiments on the reduction of carbon dioxide a mixture of hydrogen and carbon dioxide was pumped into the bomb and the latter was heated. The gaseous mixture was analyzed before and after the reaction. The data are presented in Table 65.

The following conclusions may be drawn from the data:

(1) In the presence of an excess of hydrogen with respect to carbon dioxide, complete reduction of carbon dioxide does not take place (Expts. 4, 5, 6, and 7).

(2) In the presence of an excess of carbon dioxide, hydrogen does react (Expts. 1, 2, 3, and 12).

(3) Nickel oxide and reduced nickel are equally effective as catalysts; copper oxide is much weaker in its action.

(4) When using concentrations of hydrogen and carbon dioxide corresponding to the theoretical, the reduction reaction of carbon dioxide approaches a certain limit (Expts. 3, 10, 11, and 12).

These experiments [1] are considered as only preliminary. With the limited means at my disposal (1911–1912), it was impossible for me to investigate thoroughly this most interesting reaction and all I could do was to prove that the reaction was *reversible* and that water is able to oxidize methane under these conditions. It is known at the present time as a result of the studies of a number of investigators that at ordinary pressure and high temperature (900° and above), it is easy to convert methane into hydrogen and carbon dioxide, a reaction which finds practical application in the production of hydrogen from natural gas.

Hydrogenation of Carbon Dioxide to Formic Acid; Synthesis of Formic Acid from Carbon Monoxide and Water without a Catalyst

In connection with the synthesis of methane and the investigation of the reversibility of the hydrogenation of carbon dioxide by hydrogen, I consider it appropriate to mention my experiments on the hydrogenation of carbonates and the synthesis of formic acid from carbon monoxide and water in the absence of a catalyst.

In 1913 and 1914, Starynkewitsch and I [2] made experiments on the hydrogenation of sulphuric acid, nitric acid, and salts of

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[1] A. Benedictov participated in this work.

[2] Ipatieff and Starynkewitsch, J. Russ. Phys. Chem. Soc., *46*, 172 (1914); Bull. acad. sci. Russ., 119, (1918); Ber., *56*, 1663 (1923).

TABLE 65

REDUCTION OF CARBON DIOXIDE

EXPT. No.	SUBSTANCE	CATALYST	PRESS., ATMS.		T., °C.	TIME, HRS.	ANALYSIS OF GAS						
							Before Expt.			After Expt.			
			Start	End			CO_2	O	H	CO_2	O	H	CH_4
1	CO_2 30 Atm. H_2 12 Atm.	NiO	42	20	410	30	80.2		19.6	77.4		1.2	22.0
2	CO_2 20 Atm. H_2 22 Atm.	NiO	42	19	410	30	40.0		59.0	58.1		5.6	35.6
3	CO_2 16 Atm. H_2 27 Atm.	NiO	42	20	410	30	19.0		81.0	20.1		13.2	66.5
4	CO_2 11 Atm. (2 Lit.)	Ni Redu.	100	18	394	21	4.0	3.2	82.0	4.0	3.0	6.2	75.1
5	CO_2 9 Atm. (2 Lit.)	Ni Redu.	119		390	20	1.3	2.4	86.0	0.4	0.8	61.6	34.2
6	CO_2 11 Atm. (2.5 Lit.)	Ni Redu.	103	38	385	21	5.6	2.4	82.0	0.8	0.8	50.2	44.8
7	CO_2 11 Atm. (2.5 Lit.)	Ni Redu.	110	30	404	20	5.2	2.4	82.4	0.6	1.2	25.8	68.1
8	CO_3 13 Atm. (3.0 Lit.)	Ni Redu.	85	24	410	20	6.4	2.8	81.8	8.4	0.8	8.2	74.2
9	CO_2 13.5 Atm. (2.75 Lit.)	Ni Redu.	90	21	402	20	12.0	2.8	68.0	3.6	0.8	12.8	80.2
10	CO_2 14 Atm. (4 Lit.)	Ni Redu.	100	21	410–420	22	10.0	0.8	85.0	7.0	1.0	9.0	78.3
11	CO_2 15 Atm. (4.5 Lit.)	Ni Redu.	100	21	420	22	13.2	2.0	83.0	7.0	0.4	7.0	84.5
12	CO_2 14 Atm. (3 Lit.)	NiO	80	19	420	18	20.7	1.0	74.3	13.2	1.6	11.6	65.4
13	CO_2 17 Atm. (4.5 Lit.)	CuO	100	61	470	20	14.2	2.5	74.0	15.0	0.9	17.0	62.2
14	CO_2 19 Atm. (4.5 Lit.)	CuO	100	68	460	27	14.9	2.8	72.7	18.0	1.2	12.0	63.8

carbonic acid in the laboratory of the Artillery Academy. These experiments showed that sulphuric acid is reduced to hydrogen sulphide, nitric acid to ammonia, and water solutions of alkali carbonates to formates in the absence of a catalyst.

$$KHCO_3 + H_2 \rightarrow HCOOK + H_2O$$

For various reasons, this work was not published in the Communications of the Academy of Science until 1917 and it was not until 1923 that it appeared in German. In order to develop the theory of the displacement of metals from solutions by hydrogen under the influence of hydrogen ions it was necessary to investigate the displacement of metals under the influence of another gas, namely, carbon monoxide.

For this purpose, C. Freitag and I studied the action of carbon monoxide upon a solution of copper sulphate on heating under pressure. Experiments showed that the displacement of copper from its solution occurs in a manner entirely different from what might be anticipated. The data which we have at our disposal permit us to explain all the reactions which occur in this case.

In the high pressure apparatus a quartz tube was placed containing normal, half-normal, and tenth-normal solutions of copper sulphate. Carbon monoxide was then pumped in, the tube being closed loosely with a glass cover. The pressure of the carbon monoxide varied from 20 to 100 atmospheres, the temperature from 160 to 220°, and the time of the heating was 16 hours, at the end of which time the solutions were practically colorless. In a neutral solution of copper sulphate, separation of crystalline copper was observed, but only at concentrations above half normal. The colorless solutions assumed a bluish coloration on exposure to air and this phenomenon occurred much more rapidly on heating, separation of crystalline copper being observed. Microscopic examination of the copper which separated from the solutions showed that it contained considerable crystalline copper sub-oxide. The colorless solutions containing the salts of copper sub-oxide decolorized potassium permanganate solution and used up more permanganate than was necessary for the oxidation of the salt of copper sub-oxide to the salt of copper oxide. This induced us to look for some other substance in the solution which was oxidized by potassium permanganate. Analysis of the residual gas showed the presence of 10% of carbon dioxide and 4.3% of hydrogen.

Basing our supposition on the data obtained, it was inferred that the separation of metal from the solution is promoted also by the nascent hydrogen which is liberated from the formic acid formed under these conditions from carbon monoxide and water.

$$H_2O + CO \rightarrow HCOOH$$
$$HCOOH \rightarrow 2H + CO_2$$

Therefore the reduction reaction should read as follows,

$$CuSO_4 + (HCOOH) \rightarrow Cu + H_2SO_4 + CO_2$$
$$2CuSO_4 + 2H \rightarrow Cu_2SO_4 + H_2SO_4$$

and we should have the sulphate of the sub-oxide and also a small amount of metallic copper. But, under the influence of heating, the sulphate of the sub-oxide decomposed to give metallic copper:

$$Cu_2SO_4 \rightarrow Cu + CuSO_4$$

leaving only copper sulphate in the solution. Since this solution of copper sulphate is oxidized by potassium permanganate it must contain a certain amount of formic acid or of the sulphate of copper sub-oxide. To test our hypothesis, that under these conditions formic acid is formed, we performed the synthesis of formic acid from carbon monoxide and water under pressure.

Carbon monoxide and the purest water were used for the experiment which was made in a transparent quartz tube so as to eliminate the presence of alkali. Experiment showed that with an initial pressure of 22 atmospheres of carbon monoxide and a temperature of 160°, no formic acid was obtained. Only when the initial pressure of carbon monoxide was at least 100 atmospheres at a temperature of 160–170°, did we prove by titration that the water had been converted into a $1/10\ N$ solution of formic acid. We also proved the presence of formic acid by oxidation with potassium permanganate in alkaline solution and by the preparation of its silver salt. This was the first experiment on the synthesis of formic acid from carbon monoxide and water without the participation of a catalyst.

In the presence of copper sulphate, a larger amount of formic acid was formed, the copper salt serving as a catalyst in this reaction.[1]

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[1] Ipatieff and Freitag, Chemie et Industrie. Congrès Paris, Chemie Industr. (1927) November.

HYDROGENATION OF TETRAPHENYLMETHANE

Hydrogenation of triphenyl carbinol under pressure gave us [1] a crystalline product which, according to analysis, was tricyclohexylmethane. We had thought, by analogy that from *tetraphenylmethane* we would obtain tetracyclohexylmethane, and the formation of this substance became the aim of our work. Besides, it was also interesting to test the stability of the bonds between the central carbon atom and the cyclohexyl radicals. Theoretically, it might be expected that we would obtain tetracyclohexylmethane,

$$(C_6H_5)_4C + 12H_2 \rightarrow (C_6H_{11})_4C,$$

but actually our expectations were not realized. The reaction was carried out in the high pressure apparatus at 275–285° but tetracyclohexylmethane was not obtained. If it was formed during the reaction, it decomposed into cyclohexane and tricyclohexylmethane and the latter may decompose still further to give cyclohexane and dicyclohexylmethane:

$$(C_6H_5)_4C + 13H_2 \rightarrow C_6H_{12} + (C_6H_{11})_3CH$$

$$(C_6H_{11})_3CH + H_2 \rightarrow C_6H_{12} + (C_6H_{11})_2CH_2$$

We found the same to be true when we studied the hydrogenation of hydroxytetraphenylmethane (see further):

$$\begin{array}{ll} HOC_6H_4(C_6H_5)_3C + 13H_2 & HOC_6H_{11} + (C_6H_{11})_3CH \\ \rightarrow C_6H_{12} + & {}_{11}\text{—}CH_2\text{—}C_6H_{11} \end{array}$$

In other words, the phenolic hydroxyl group did not change the course of the reaction.

The data obtained from the high pressure catalytic hydrogenation of triphenylmethane, triphenyl carbinol (see further), tetraphenylmethane, and para-hydroxytetraphenylmethane led us to the conclusion that the crystalline product obtained was *tricyclohexylmethane.* Tetracyclohexylmethane was not formed because of its instability and a greater affinity of the carbon atom for hydrogen than for the cyclohexyl radical. In all cases, hydrogenation was continued until the pressure no longer fell (6–8 days).

Hydrogenation of Tetraphenylmethane.—This hydrocarbon was obtained from triphenyl carbinol by way of aminotetraphenylmethane (by diazotization followed by decomposition of the diazo compound by boiling alcohol) according to the method of Ullman and Munberg.[1] The product was a yellowish powder melting at 280–281°.

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[1] Ipatieff and Dolgov, Bull. soc. chim., *39*, 1456 (1926).

The hydrogenation was carried out in an 800-cc. high pressure apparatus. Twenty-five grams of tetraphenylmethane was dissolved in 100–150 cc. cyclohexane, 2.5 g. nickel oxide was added, and finally 100 atmospheres of hydrogen; the temperature used for the reaction was 275–285°. The reaction velocity was sufficiently high at the beginning, but it diminished gradually towards the end. Hydrogen was pumped into the apparatus twice and the experiment lasted six days.

After removal of the solvent, the product of the reaction was a colorless, transparent liquid, which was separated into two fractions by distillation.

		Pressure	
		20 mm.	760 mm.
First Fraction,	b.p.,	130–150°	250–260°
Second Fraction,	b.p.,	205–206°	330–333°

The first fraction, a mobile liquid, yielded a product boiling at 251–253° which analyzed for *dicyclohexylmethane.*

Anal. Calcd. for $C_{13}H_{24}$: C, 86.6; H, 13.4; M.R., 57.73. Found: C, 86.2; H, 13.7; d_0^{20}, 0.8743; n_D^{20}, 1.4755; M.R., 57.53.

The second fraction (b.p., 330–333°) was a thick, viscous liquid which after standing for two days, deposited a small amount of crystals. However, since it gave a red coloration with sulphuric acid and reacted with nitrating mixture it was doubtless an incompletely hydrogenated product and contained at least one benzene ring. Therefore, it was subjected to a second hydrogenation which yielded a very thick oil which readily crystallized. After recrystallization from methyl alcohol, white crystals were obtained, similar to *tricyclohexylmethane.*

Anal. Calcd. for $C_{19}H_{34}$: C, 87.0; H, 13.0; M.R., 83.3; mol. wt., 262. Found: C, 87.1; H, 12.7; d_0^{50}, 0.9274; n_D^{50}, 1.4967; n_D^{40}, 1.4986; M.R., 82.5; mol. wt. (in benzene), 259.

The hydrocarbon was slightly soluble in methyl alcohol, ethyl alcohol, and glacial acetic acid; readily soluble in benzene and cyclohexane. It was not acted upon by potassium permanganate, nitrating mixture, or sulphuric acid.

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[1] Ullman and Munberg, Ber., *36*, 404 (1904).

COPPER OXIDE CATALYST

HYDROGENATION OF ALIPHATIC COMPOUNDS WITH A DOUBLE BOND IN THE PRESENCE OF COPPER OXIDE

When olefin hydrocarbons are passed over reduced copper in the presence of hydrogen, hydrogenation of the double bond occurs and paraffinic hydrocarbons [1] are formed. This hydrogenation is effective only for those olefins which contain a double bond attached to the CH_2 radical; other olefins, such as trimethylethylene, beta-hexene, and others, do not add hydrogen in the presence of copper. Similarly, hydrogenation, in the presence of reduced copper, was also shown by Sabatier and Senderens to take place with cyclic hydrocarbons containing an ethylenic linkage in the side chain. However, conversion of the double bond into a single bond by the addition of hydrogen may be greatly facilitated by using reduced nickel or nickel oxide although there are some cases in which these catalysts cannot be employed. For example, if a nickel catalyst is used for the hydrogenation of the double bond in the side chain of an unsaturated cyclic compound there is simultaneous hydrogenation of both side chain and the unsaturated cyclic nucleus. With these conceptions as a beginning, I undertook an investigation on the high pressure hydrogenation in the presence of copper oxide of certain compounds containing a double bond. It was found that copper oxide [2] (as indicated by experiments with unsaturated hydrocarbons and with acids) is a good catalyst for the hydrogenation of the double bond and that it is more active than reduced copper.

Hydrogenation of Ethylene.—Two or three grams of copper oxide was placed in the high pressure apparatus and then the bomb was filled with a mixture of 67.3% of ethylene and 32.7% of hydrogen at 60 atmospheres pressure. After heating the apparatus to 180°, a very slow decrease in pressure was observed. At the end of six hours the reaction had ceased and during the following twelve hours no change in the pressure was noticed. On cooling, the pressure in the apparatus fell to 40 atmospheres and analysis showed that the gas contained ethylene (originally taken in excess) and ethane, and there was probably a small amount of hydrogen and methane also.

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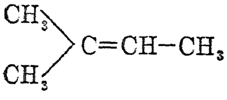
[1] Sabatier and Senderens, Ann. chim. phys. (8), *4*, 347 (1905).

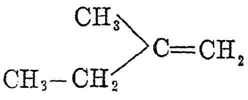
[2] Ipatieff, Ber., *42*, 2089 (1909).

An entirely different picture presented itself when, instead of using copper oxide, nickel oxide or reduced nickel was employed in the hydrogenation of ethylene under pressure. In spite of the fact that the lowest possible temperature (130°) was used, there was simultaneous addition of hydrogen to the ethylene and splitting of a part of the ethane to form methane. Thus, we always obtained a mixture of methane and ethane. At ordinary pressure the hydrogenation of ethylene in the presence of copper oxide proceeds very slowly and, therefore, this reaction has no practical application.

Hydrogenation of Trimethylethylene.—Freshly distilled commercial trimethylethylene boiling at 36–38° was used in this experiment. It is well known that this material consists chiefly of two isomers, namely:



and



Forty grams of the amylene and 3 g. of copper oxide were placed in the apparatus together with hydrogen at 100 atmospheres. This hydrogenation was made at 300°, and was finished in 12 hours. The product neither decolorized potassium permanganate solution nor added bromine. It consisted almost exclusively of a saturated hydrocarbon, *isopentane*, boiling at 30–32°. Consequently, the hydrogenation of the double bond, independent of its configuration, proceeds to completion in the presence of reduced copper or copper oxide under pressure, while at ordinary pressure the structure of the hydrocarbon greatly influences the course of the hydrogenation.

In the study of this reaction it was observed that besides the chief product of the reaction, a very small amount of a substance was formed which analysis showed to be *amyl alcohol.* After distilling off the hydrocarbon, about 1 g. of liquid remained which distilled at 100°. This liquid was soluble in water and it did not decolorize potassium permanganate solution nor add bromine. However, it did evolve hydrogen when treated with sodium and it had the odor of the tertiary alcohol *dimethylethyl carbinol.* The small amount of alcohol at my disposal did not permit its isolation in the pure state but analysis and the properties enumerated above indicated that it was an amyl alcohol.

The formation of alcohol from amylene in the presence of copper oxide is of the greatest interest since its formation represents the catalytic hydration of an olefin. Experiments subsequently made by C. Freitag and myself on the hydration of ethylene and of amylene in the presence of hydrochloric acid and very dilute sulphuric acid under pressure showed us that hydration occurs quite readily and that we may obtain ethyl ether and alcohol from ethylene. At the present time, patents exist for obtaining alcohol from ethylene and water using high pressures (200 atmospheres) and temperatures around 400°, and such catalysts as thorium oxide, phosphoric acid supported on active carbon, and others. (Slade, Brit. Pat., 1928.)

Hydrogenation of Oleic Acid.—The hydrogenation of sodium oleate in the presence of copper oxide in the high pressure apparatus yielded solid stearic acid melting at 64–67°.[1]

Hydrogenation of Tetrahydrobenzene.—In order to make possible the hydrogenation of the double bond in cyclic compounds, experiments with tetrahydrobenzene (C_6H_{10}) were carried out in the presence of copper oxide. The starting material was obtained catalytically from cyclohexanol by the removal of water from the latter by means of alumina [2] in the high pressure apparatus. The tetrahydrobenzene was then heated with hydrogen in the presence of reduced copper or copper oxide. The maximum pressure in the apparatus was 187 atmospheres and the temperature was 400°. The duration of the experiment was 12 hours. In spite of long heating and high temperature and pressure, hydrogenation did not occur and unchanged starting material was recovered (b.p., 80–81°) along with a very small amount (1 g.) of a polymerization product. This negative result led to the conclusion that copper oxide cannot hydrogenate the double bond in cyclic compounds, even under pressure. However, it is most important to note the fact that this attempted hydrogenation of tetrahydrobenzene in the presence of copper oxide was performed in a bronze-copper apparatus. In a later chapter I shall mention certain substances, e.g., the walls of the containing vessel, which sometimes exercise a very great influence on the course of catalysis. (See chapter on

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[1] Ipatieff, Ber., *42*, 2091 (1909).

[2] Ipatieff, J. Russ. Phys. Chem. Soc., *37*, 1926 (1905).

"Joint Action of Catalysts.") In other words there is the possibility of *activating the catalyst* by adding to it another catalyst which, taken separately, is unable, in many cases, to produce the given reaction.

HYDROGENATION OF TERPENES [1]

In the presence of reduced nickel catalysts, as shown by Sabatier and Senderens,[2] hydrogenation of terpenes takes place to give either naphthenic hydrocarbons or hydroaromatics depending upon the structure of the terpene. Thus, for example, limonene adds four hydrogen atoms to form hexahydrocymene, whereas pinene adds two hydrogens to give a hydrocymene of composition $C_{10}H_{18}$ with one double bond in the nucleus. Sabatier and Senderens also investigated the action of reduced copper in the hydrogenation of limonene and found that copper was a catalyst; limonene added two hydrogens to the double bond in the aliphatic side chain, the product of the reaction being menthene, $C_{10}H_{18}$.

Vavon [3] studied the hydrogenation of certain terpene hydrocarbons in the presence of platinum black. Pinene, when shaken with hydrogen in the presence of this catalyst, gave the hydrocarbon $C_{10}H_{18}$, and limonene added four atoms of hydrogen to form $C_{10}H_{20}$. The properties of these hydrocarbons are the same as those of the hydrocarbons obtained by Sabatier and Senderens by the hydrogenation of pinene and limonene.

Since information on the hydrogenation of terpenes was meager, it was decided to study the hydrogenation of various types of terpenes, under pressure and in the presence of various catalysts, in the attempt to establish some regularity between the course of the reaction and the structure of the terpene. Copper oxide was employed in most of these hydrogenation experiments, the aim being to determine the possibility of hydrogenating the double bond in the nucleus and also to follow the course of the reaction in the hydrogenation of terpenes having two double bonds.

Hydrogenation of Limonene.—The limonene used in these experiments boiled at 176°; d_{20}, 0.8575; $(\alpha)_D = 75.50°$. The limonene, 25 to 50 g., was placed in the iron tube of the high pressure apparatus and hydrogen was pumped in to about 100 atmospheres, after

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[1] Ipatieff, Ber., *43*, 3546 (1910).
[2] Sabatier and Senderens, Compt. rend., *132*, 1333 (1901).
[3] Vavon, Compt. rend., *149*, 197 (1910).

TABLE 66

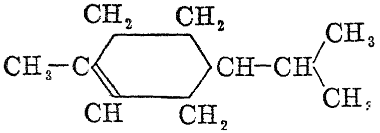
HYDROGENATION OF TERPENES

EXPT. No.	SUBSTANCE	CATALYST	PRESSURE, ATMS.		T., °C.	TIME, HRS.	d_{20}	α	ANALYSIS				PRODUCT OF REACTION, B.P.
									Found		Calcd.		
			Initial	Final					% C	% H	$C_{10}H_{18}$	$C_{10}H_{20}$	
1	Limonene	CuO	110	80	280	18		18.20	87.3	12.9	80.9	85.7	173–176 176–185
2	Limonene	CuO	120	74	300	6			87.4	12.9	13.08	14.3	172–174 174–176
3	Dihydro-carbon	CuO	125	90	310	12	0.8016	0	85.9	14.1			169–170 (Note 1)
4	Limonene	Cu	129	78	330	15							167–172 (Note 2)
5	Hydro-limonene	Cu	120	103	320	12	0.7965	0	86.3	11.1			169–170 (Note 1)

Note 1: Does not react with nitrating mixture.
Note 2: Does react with nitrating mixture.

which the apparatus was heated at constant temperature until the pressure remained constant. The results are summarized in the preceding table.

As seen above, the hydrogenation of limonene is promoted by copper oxide but not by copper, the reaction product being menthane ($C_{10}H_{18}$) or the hydroaromatic compound $C_{10}H_{20}$. Copper oxide is an excellent catalyst inasmuch as it functions at low temperature. According to Expts. 1, 2, and 4, the product of the first hydrogenation of limonene was a liquid (probably a mixture of several isomers) which gave no precipitate with nitrosyl chloride. It yielded a liquid bromide when treated with bromine, and decolorized potassium permanganate solution. Its analysis indicated the formula $C_{10}H_{18}$. Evidently, the hydrogenation is limited to the addition of two hydrogen atoms to the double bond of the aliphatic chain with the formation of the following hydrocarbon.



When this hydrocarbon was subjected to a second hydrogenation, two hydrogen atoms added to the double bond in the nucleus and menthane (p-methylisopropylcyclohexane) was formed, identical with the hydrocarbon obtained by Sabatier and Senderens with reduced nickel, and with that of Vavon, using platinum black for the hydrogenation of limonene at ordinary pressure. The yield of menthane was quite satisfactory, a very small amount of polymerization product being also formed.

Hydrogenation of Pinene.—For these experiments, a fraction of a French turpentine was used which had the boiling point 155–156°, d_{20}, 0.8546, $(\alpha)_c$, 33.48°, $(\alpha)_D$, 41.10, n_D^{20}, 1.47488. For each experiment, 30 to 50 g. of hydrocarbon and 3 to 5 g. of catalyst were placed in the high pressure apparatus together with 110–120 atmospheres of hydrogen. In the presence of *iron,* hydrogenation did not take place, but the tetramethylene ring opened and there was isomerization into dipentene and also the formation of polymerization products. From 50 g. of pinene, a fraction boiling at 170–180° was obtained; 25 g. of which remained unchanged during a second hydrogenation. According to its reactions it was evidently *dipentene.*

In the presence of copper oxide, pinene was hydrogenated, the amount of hydrogen added depending on the temperature. At 265° the product was $C_{10}H_{18}$, at 240° incompletely hydrogenated dipentene resulted, while at 280–290° two molecules of hydrogen were added with the formation of a hydrocarbon with d_{20}, 0.7949 and composition corresponding closely to that of *menthane.*

Anal. Calcd. for $C_{10}H_{20}$: C, 85.7; H, 14.3. Found: C, 85.9; H, 14.1.

In spite of its satisfactory analysis this hydrocarbon decolorized potassium permanganate, reacted quite vigorously with nitrating mixture, and distilled over a wide range (163–170°). It could not be pure menthane and, therefore, it was subjected to a second hydrogenation from which a colorless liquid was obtained. The greater part of this material distilled at 163–170° and had the same properties and analytical data as the product of the first hydrogenation. However, it reacted less vigorously with permanganate and nitrating mixture, but when heated with the latter, the reaction was vigorous.

On the assumption that the product of hydrogenation contained some substance which could not be hydrogenated in the presence of copper oxide, an attempt was made to remove this material by a 5% solution of potassium permanganate. A mixture of permanganate and hydrogenation product (1st and 2nd) was stirred 6–8 hours. The unchanged hydrocarbon, after extraction with ether and removal of the ether, distilled as before at 163–170°, and also reacted as before with potassium permanganate solution and nitrating mixture. The permanganate-treated material was divided into two fractions, (1) b.p., 163–166°, (2) b.p., 166–169°, and each was analyzed. The results of analysis emphasized the fact that oxidation had effected no change.

Anal. Found: (1) C, 85.9; H, 14.3. (2) C, 85.9; H, 14.1.

The abnormal behavior of nitrating mixture cannot, therefore, be ascribed to the presence of another hydrocarbon containing a double bond. In order to study more closely the product of the repeated hydrogenation of pinene, a triple hydrogenation was made. In the first hydrogenation, 86 g. of pinene yielded 74 g. of product boiling at 163–170° and 12 g. of higher boiling material. Hydrogenation of the 163–170° fraction gave 61 g. of product boiling at 163–170° and only 2 g. of polymerization products. Finally, a third hydrogenation of the 163–170° fraction gave a hydrocarbon (d_{20}, 0.7949) which distilled at 163–170°, leaving in the distillation flask about 1 g. of higher boiling product.

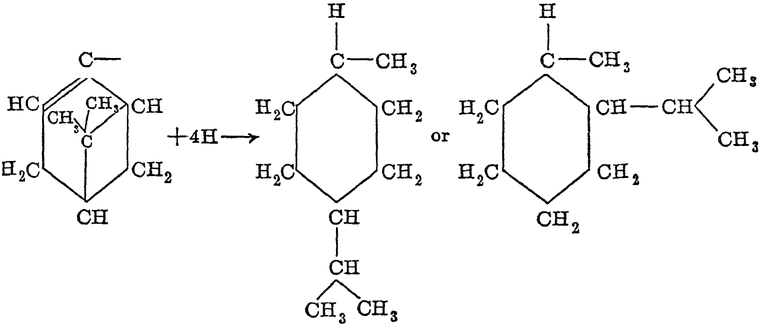
Anal. Calcd. for $C_{10}H_{20}$: C, 85.7; H, 14.3. Found: C, 85.4; H, 14.5.

The action of nitrating mixture upon the product of the third hydrogenation was quite weak but some heat was evolved when the hydrocarbon was added to the nitrating mixture, an effect not to be expected with a naphthenic hydrocarbon. However, nitrating mixture reacted energetically with the residue in the flask boiling above 170°. From this it may be assumed that this substance represents a by-product, present in relatively large amount in the product from the first hydrogenation but decreasing in amount on subsequent treatment with hydrogen.

In the hydrogenation of trimethylethylene with copper oxide, there was formed, besides the normal product, the saturated hydrocarbon isopentane and also a by-product due to the addition of water to the olefin, which by analysis and its properties showed itself to be a tertiary alcohol. The formation of the high boiling product in the hydrogenation of pinene might also have been due to the hydration of the double bond in the ring, in which case the high boiling material might be an alcohol or a ketone, which, of course, would react with nitrating mixture.

In the case of the hydrocarbon $C_{10}H_{20}$, because of the wide boiling range, we must assume it to be a mixture of isomers. Isomerization into dipentene occurred on heating pinene at 250–260° in an iron tube without a catalyst. In the presence of a catalyst the following reactions probably take place: (1) hydrogenation of the double bond in the ring; (2) opening of the tetramethylene ring with simultaneous hydrogenation; (3) isomerization of pinene into dipentene followed by the addition of one or two molecules of hydrogen to the latter. The final result of this process may be the formation of dihydropinene, or of dihydrodipentene by the addition of one molecule of hydrogen, or of menthane by the addition of two molecules of hydrogen. The menthane would consist of two isomers, the relative amounts depending upon the manner in which the cyclobutane ring opens; that is, the methyl group may be either ortho or para with respect to the isopropyl group.

It is possible to explain the wide range of the boiling point of the menthane obtained as due to the presence of both isomers. This explanation is the more logical inasmuch as the menthane obtained by the hydrogenation of limonene is uniform and distills at 169–170°.



In the presence of *reduced copper*, the hydrogenation of pinene proceeds in the same way as in the presence of copper oxide, with the exception that at 280–290° with reduced copper a product is obtained which boils at 169–175° whose composition is $C_{10}H_{18}$, whereas the product obtained in the presence of copper oxide at the same temperature is $C_{10}H_{20}$. Only when the temperature is raised to 300° does hydrogenation in the presence of copper proceed further. But, in order to obtain the hydrocarbon $C_{10}H_{20}$ (b.p., 166–169°; d_{20}, 0.7976), it is necessary to hydrogenate twice.

In the presence of *nickel oxide*, the addition of hydrogen to pinene under pressure proceeds more rapidly and at a lower temperature than with copper oxide, menthane (b.p., 163–169°; d_{20}, 0.8028) being obtained. Also the amount of higher boiling products is only half that obtained with copper oxide. The menthane gave the following analytical data:

Anal. Calcd. for $C_{10}H_{20}$: C, 85.7; H, 14.3. Found: C, 85.8; H, 14.6.

The product of the third hydrogenation of pinene in the presence of copper oxide was acted upon also by nitrating mixture which colored the hydrocarbon yellow on heating. The product boiling at 163–169° was subjected to a second hydrogenation using nickel oxide. The product resulting from the double hydrogenation had the same properties as that from a single hydrogenation and gave the same reaction with nitrating mixture.

In order to compare the menthane obtained by the hydrogenation of pinene in the presence of various catalysts with the menthane from cymene, the latter was hydrogenated in the presence of nickel oxide under pressure at 240–250°. Methylisopropylcyclohexane (b.p., 168–170°; d_{20}, 0.8038; C, 85; H, 14.5) was obtained, which was identical with the menthane obtained from pinene except that it did not react with nitrating mixture.

HYDROGENATION OF PHENOLS

As already described,[1] the use of high pressures readily permits the hydrogenation of phenols and naphthols in the presence of nickel oxide. At the present time, the hydrogenation of phenols on a commercial scale is conducted by my method, the reaction proceeding rapidly and resulting in complete hydrogenation of phenols.

Experiments were also made on the hydrogenation of phenols containing an *unsaturated side chain.* It may be predicted from my experiments on the hydrogenation of unsaturated side chains, as well as of nuclear double bonds, that copper oxide may be used with success at a temperature of 270–300° under which conditions the aromatic ring will not undergo hydrogenation. Experiments made with various phenols and their corresponding ethers, e.g., anisole, eugenol, etc., in the presence of nickel catalysts showed simultaneous saturation of both the side chain and the nucleus.

The addition of hydrogen to the double bond takes place readily at 95° and the speed of reaction is increased by stirring. At the present time, I use a mechanical stirrer (already described) very simply constructed and not easily damaged in use, which permits working under pressures of 50 to 70 atmospheres. It is much more convenient to work with this stirrer than with that of Werhowsky which is operated by an electromagnet. Werhowsky's stirrer permits working under high pressures, but at high temperatures with volatile substances, its action becomes difficult. In the laboratory, pressures of 30 to 50 atmospheres are sufficient as the reaction which I studied proceeds well at 20 and 30 atmospheres. With an initial pressure of 100 atmospheres it was possible to hydrogenate large amounts of material without further addition of hydrogen.

After hydrogenation of the side chain double bond at 100°, the reduced nickel was able to hydrogenate the benzene ring at 185–190°. At this temperature and pressure, the addition of six atoms of hydrogen to the aromatic nucleus took place and in all cases investigated (without solvent) there was also reduction of one hydroxyl or methoxyl group.

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[1] Ipatieff, J. Russ. Phys. Chem. Soc., *37*, 1295 (1905).

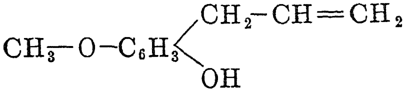
Hydrogenation of Anethole.—Thirty grams of anethole, $CH_3—CH{=}CH—C_6H_4OCH_3$, together with 3 g. of reduced nickel, were placed in a glass tube which was placed in the high pressure apparatus under 50 atmospheres hydrogen pressure. The reaction was continued with stirring at 95° for four hours. The reaction product distilled at 212–214° at 766 mm. (d_{20}, 0.9462). It did not decolorize potassium permanganate solution, did not add bromine, and according to the analysis was *dihydroanethole.*

Anal. Calcd. for $C_{10}H_{14}O$: C, 80.0; H, 9.3. Found: C, 80.4; H, 9.1.

When dihydroanethole was subjected to a second hydrogenation in the presence of nickel at 200° for 20 hours with stirring, the product had all the properties of hexahydropropylbenzene; b.p., 160° (760 mm.); d_{20}, 0.8082. Thus, through hydrogenation, a splitting-off of the methoxyl group took place.

Anal. Calcd. for C_9H_{18}: C, 85.7; H, 14.3. Found: C, 86.1; H, 14.1.

Hydrogenation of Eugenol.—Eugenol,



$$CH_3{-}O{-}C_6H_3\begin{cases}CH_2{-}CH{=}CH_2\\ OH\end{cases}$$

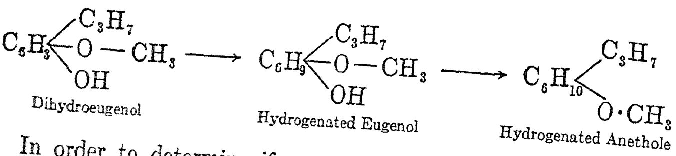
was subjected to hydrogenation under the same conditions as described for anethole. After 2 to 3 hours at 92°, an excellent yield of dihydroeugenol was obtained which did not decolorize potassium permanganate solution nor add bromine. Its boiling point was 246° (762 mm.) and d_{20}, 0.9209.

Anal. Calcd. for $C_{10}H_{14}O$: C, 72.2; H, 8.6. Found: C, 72.4; H, 8.6.

When dihydroeugenol was subjected to further hydrogenation at 195° for a period of 7 hours, a product was formed which distilled at 210–235° (766 mm.). Analysis of the fraction boiling at 215–225° at 766 mm. (d_{20}, 0.9207) gave the following results.

Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.7; H, 11.6. Calcd. for $C_{10}H_{20}O$: C, 76.9; H, 12.8. Found: C, 74.9; H, 12.7.

Analysis showed that not only was the normal product of the hydrogenation of dihydroeugenol obtained, octahydroeugenol, but also some hexahydroanethole originating through the reduction of the hydroxyl group.



Dihydroeugenol

Hydrogenated Eugenol

Hydrogenated Anethole

In order to determine if a normal product of hydrogenation would be obtained if two methoxyl groups were present, the methyl ether of eugenol was hydrogenated.

This substance, $C_3H_5—C_6H_3(OCH_3)_2$, gave after the first hydrogenation at 95° for two hours with stirring, the *dihydromethyl ether;* b.p., 244–245° (763 mm.); d_{20}, 1.0105.

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.3; H, 8.9. Found: C, 75.6; H, 9.2.

The dihydromethyl ether of eugenol was given a second hydrogenation at 200–210° for 10 hours with stirring. The product distilled completely at 195–210° and the fraction boiling at 200–210° at 759 mm. (d_{20}, 0.9027) gave the following analytical data.

Anal. Calcd. for $C_{10}H_{22}O_2$: C, 71.0; H, 11.8. Calcd. for $C_{10}H_{20}O$: C, 76.9; H, 12.8. Found: C, 77.3; H, 13.0.

The analytical data leaves no doubt that the hydrogenation of the dihydromethylether of eugenol involves a splitting off of the methoxyl group and that octahydroanethole is the product of the reaction.

$$C_3H_7—C_6H_3(OCH_3)_2 \rightarrow C_3H_7—C_6H_{10}O—CH_3$$

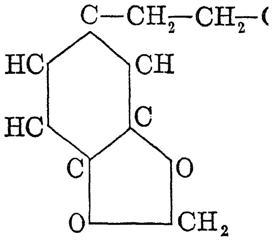
The reduction of the methoxyl group proceeds much more rapidly than that of the hydroxyl group, and in this case only, was the hydrogenated monohydric phenol obtained.

Hydrogenation of Safrole.—The addition of two atoms of hydrogen to safrole took place at 93° in 2 hours, the product boiling at 228–230° (747 mm.). According to its properties and analysis, the product was *dihydrosafrole* (d_{20}, 1.0694).

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.2; H, 7.3. Found: C, 73.3; H, 7.3.

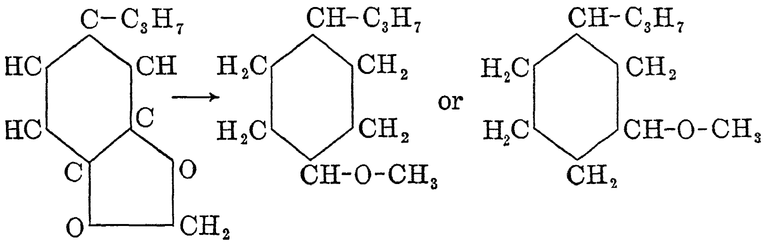
When the hydrogenation of safrole was carried out at ordinary pressure with stirring and continuous passage of hydrogen for four or five hours at a temperature of 140–160°, no addition of hydrogen occurred in spite of the change in the boiling point of the safrole. The product distilled at 233–245° and its analysis gave the following data.

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.1; H, 6.2. Found: C, 74.1; H, 6.1.



Hydrogenation of Isosafrole.—The hydrogenation of isosafrole by the addition of two hydrogen atoms should give a product identical with dihydrosafrole since isosafrole differs only in the position of the double bond in the side chain. Experiment substantiated this assumption since the dihydrosafrole obtained had a boiling point of 229–230° and analysis gave figures corresponding to the formula $C_{10}H_{12}O_2$.

By further hydrogenation of dihydrosafrole in the presence of reduced nickel, not only did six atoms of hydrogen add, but further reduction took place. According to the analysis, we must assume that isomers of *octahydroanethole* were formed.



The hydrogenation of dihydrosafrole was made at 180° for 10–12 hours with stirring. The product distilled at 207–212°. The fraction boiling at 208–209° at 746.7 mm. (d_{20}, 0.9096) was taken for analysis.

Anal. Calcd. for $C_{10}H_{20}O$: C, 76.9; H, 12.8. Found: C, 76.1; H, 12.4.

The slightly low carbon and hydrogen percentages of the product may be explained by the presence of small amounts of the ether of the dihydric phenol, $HOC_6H_9(OCH_3)C_3H_7$ (C, 69.77%; H, 11.62%). This experiment shows the conversion of dihydrosafrole into a monohydric naphthenic alcohol with the removal of one atom of oxygen by hydrogenation.

HYDROGENATION OF POLYHYDRIC PHENOLS [1]

By the hydrogenation of hydroquinone in the presence of nickel oxide or reduced nickel in the high pressure apparatus, we had previously [2] obtained cis- and the trans-quinite. However, because of the slowness of the reduction and the small yield of *quinite*, due to the ready loss of water and partial tarring of hydroquinone at 240°, it was thought best to use the simple ethers of phenols for hydrogenation, with the supposition that the methoxyl group might not split off as readily, and that there would not be much tar formation.

Experiments carried out with various phenols only partially justified these expectations. While the yield of the normal hydrogenated product was better, the occurrence of side reactions complicated the separation of the products. The conclusions drawn from the experiments on the hydrogenation of phenols with side chains containing a double bond might also be applied here.

Hydrogenation of Guaiacol.—For the hydrogenation of guaiacol in the high pressure apparatus, the charge consisted of 30 g. of guaiacol, 3 g. of nickel oxide, and 100 atmospheres of hydrogen. Reaction was allowed to take place at 220–240° over a period of 12 to 15 hours, at the end of which time the pressure in the apparatus had become constant. The liquid product did not contain tarry substances, but it distilled over a wide range, (1) 80–170°; (2) 170–192°; (3) 192–210°.

On the basis of the distillation data, it could not be inferred that complete hydrogenation of guaiacol had occurred, but negative results with the characteristic tests for guaiacol, using potassium permanganate and ferric chloride, were sufficiently convincing that guaiacol was not present in the product.

In the first fraction (the smallest) the presence of cyclohexane was easily shown. This product resulted from the complete reduction of guaiacol with removal of hydroxyl and methoxyl groups.

The second fraction, which was larger, gave the following analytical data:

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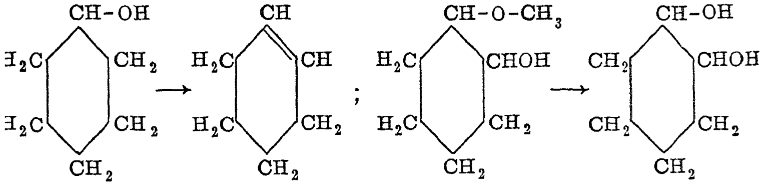
[1] This work was carried out together with Lugovoy.

[2] Ipatieff, J. Russ. Phys. Chem. Soc., *37*, 1295 (1905).

Anal. Calcd. for $C_7H_{14}O_2$: C, 64.6: H, 10.7. Found: C, 69.1; H, 11.5.

The data necessitated the conclusion that either a hydrogenated anisole or a cyclohexanol must be admixed with the normal product, but hydrogenated anisole obtained in other experiments could not be present in the hydrogenated product judging from its properties and boiling point of 142–145°. All data indicated that about 50% of hexahydrophenol (b.p., 165°; C, 72%; H, 12%) was admixed with the normal product.

In order to convince ourselves of the presence of hexahydrophenol and to enable us to separate it from hexahydroguaiacol, the product was subjected to the joint action of aluminum oxide and copper oxide. The investigation of Ipatieff and Matov on the joint action of these catalysts had shown that aluminum oxide in the presence of copper oxide causes the dehydration of alcohols at a much lower temperature than that necessary with alumina alone. Therefore, the assumption was that in the present case the removal of water from the hexanol, with the formation of tetrahydrobenzene, would take place and that hexahydroguaiacol, when subjected to hydration, would be converted into hexahydrocatechol. The experimental results substantiated these expectations.



Cyclohexanol Cyclohexene Hexahydroguaiacol Hexahydrocatechol

For the experiment on dehydration, 50 g. of the hexahydroguaiacol was mixed with 2 g. of aluminum oxide and 4 g. copper oxide and this mixture was placed in the high pressure apparatus, to which 50 atmospheres of hydrogen was added. The reaction was allowed to proceed at 250° for 19 hours. In another experiment, 32 g. of hexahydroguaiacol was mixed with 1.5 g. aluminum oxide, 2.5 g. of copper oxide, and 1 g. of water, 60 atmospheres of hydrogen being pumped into the apparatus. The time of heating was 12 hours and the temperature 280°. The results of both of these experiments were identical and no tar formation was observed. The liquid product was distilled into four fractions: (1) 55–90°; (2) 90–170°; (3) 170–192°; and (4) 192–200°.

The first fraction (b.p., 55–99°) consisted principally of cyclohexane with a small amount of tetrahydrobenzene. Cyclohexane was formed due to the fact that nuclear double bonds are hydrogenated in the presence of copper oxide above 250°.

Analysis of the fourth fraction gave the following results:

Anal. Calcd. for $C_6H_{10}(OH)_2$: C, 62.1; H, 9.6. Found: C, 62.9; H, 10.1.

According to the analysis and other properties, the substance was hexahydrocatechol, contaminated, however, with a small amount of undecomposed cyclohexanol. This impure hexahydrocatechol could not be crystallized, but on long standing on a watch glass, a very small amount of crystals was obtained, but the melting point was not determined.

Analysis of the third fraction showed that the lower boiling fractions contained large amounts of undecomposed hexahydrophenol, and in order to remove it from the hydrogenated catechol, it was necessary to subject the mixture to a second dehydration. Thus, the joint action of these catalysts not only permitted dehydration at a lower temperature, but also converted the methoxyl group into the hydroxyl group.

To prove this, a series of experiments was carried out on the conversion of guaiacol to catechol under the joint influence of alumina and copper oxide, and the following optimum conditions were established.

A mixture of 25 g. of guaiacol, 1.5 g. of alumina, 1.5 g. of copper oxide, and 7 g. of alcohol (95%) was heated in the high pressure apparatus under a pressure of 50 atmospheres of hydrogen. The reaction was allowed to continue for 12 hours at 300–305°. The liquid product distilled for the greater part at 225–250° and solidified to a crystalline mass in the receiver; practically no tar formation was observed. The crystals after drying on clay plate melted at 101–104° and possessed all the properties of pyrocatechol. This reaction is reversible and under the above conditions it is possible to obtain somewhat more than a 50% yield of pyrocatechol.

When guaiacol was heated in the presence of alumina under hydrogen pressure at 300° for only 18 hours, considerable tar formation was observed and no pyrocatechol was obtained.

Hydrogenation of Anisole, $C_6H_5OCH_3$.—To clear up the nature of the products obtained in the hydrogenation of guaiacol, it was necessary to determine the properties of hydrogenated anisole, which up to that time had not been done.

There was placed in the high pressure apparatus 30 g. of anisole, 2 g. nickel oxide, and 100 atmospheres of hydrogen. The bomb was then heated at 240° for 24 hours. The liquid product was separated into fractions of the following boiling ranges: (1) 70–100°; (2) 143–145°; (3) 158–160°.

The first fraction, which was the smallest, consisted of cyclohexane. The second fraction, more than 40% of the product, was hexahydroanisole, $C_6H_{11}OCH_3$, boiling point 143–145° (753 mm.), d_{20} 0.9026.

Anal. Calcd. for $C_6H_{11}OCH_3$: C, 73.6; H, 12.3. Found: C, 74.0; H, 11.8.

The third fraction, according to its properties and analysis, was hexahydrophenol.

Anal. Calcd. for $C_6H_{11}OH$: C, 72.0; H, 12.0. Found: C, 71.7; H, 11.7.

Thus, on hydrogenating this simple ether of phenol in the presence of nickel oxide, about 50% of the normal product of hydrogenation was obtained. The rest of the hydrogenated anisole underwent scission with the formation of hydrogenated phenol a part of which was further hydrogenated to a polymethylene hydrocarbon.

The hydrogenation of the diethyl ether of catechol was conducted under the conditions described above at a temperature of 230° for 40 hours, or until the pressure in the apparatus remained constant. The liquid product of the reaction (87 g.) was distilled and the following fractions obtained: (1) 70–80°; (2) 180–190°; (3) 190–200°.

The first fraction consisted chiefly of cyclohexane. The second and the third fractions, about 50% of the product, according to their properties and analyses consisted of the normal product of the reaction, the hydrogenated diethyl ether of catechol, $C_6H_{10}(OC_2H_5)_2$, which was probably present as a mixture of the cis- and trans-isomers.

Analysis of the fraction boiling at 180–190° gave the following results:

Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.7; H, 11.6. Found: C, 69.9; H, 11.4.

Analysis of the fraction boiling at 190–200° gave the following results:

Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.8; H, 11.6. Found: C, 69.3; H, 10.8.

The *hydrogenation of the methyl ether of resorcinol,* carried out under the conditions described above, gave a smaller amount of normal product than was obtained from the ether of catechol. The boiling points of the chief fractions of the hydrogenated product, about 50% of the total amount, were: (1) 148–160°; (2) 160–200°.

Analysis of the fraction boiling at 148–160° gave the following figures:

Calcd. for $C_6H_{11}OCH_3$: C, 73.6; H, 12.3. Calcd. for $C_6H_{10}(OCH_3)_2$: C, 66.7; H, 11.1. Found: C, 72.2; H, 11.7.

Analysis of fraction 180–200°:

Calcd. for $C_6H_{10}(OCH_3)_2$: C, 66.7; H, 11.1. Found: C, 70.4; H, 11.2.

According to the boiling points of these fractions and their analyses, it must be assumed that considerable hexahydrobenzene was present, due to the removal of one methoxyl group and its replacement by an atom of hydrogen.

The *hydrogenation of the dimethyl ether of hydroquinone* yielded hexahydroanisol admixed with a considerable amount of the normal product of the reaction. The liquid product of the reaction was divided into three fractions: (1) 60–100°; (2) 130–165°; (3) 165–190°, and the analysis of the second fraction (the largest) gave the following results:

Anal. Calcd. for $C_6H_{11}OCH_3$: C, 73.6; H, 12.3. Found: C, 73.6; H, 11.0.

Generalizing from the experimental data on the reduction of dihydric phenols by hydrogen under pressure in the presence of nickel oxide, it may be stated that only in the case of the ether of catechol is simple hydrogenation obtained. In the other cases investigated one of the methoxyl groups split off to be replaced by hydrogen as is also observed in the hydrogenation of phenols with unsaturated side chains.

Hydrogenation of Benzyl Alcohol and Benzaldehyde in the Presence of Iron.[1]—I had previously shown [2] that aliphatic aldehydes and ketones are reduced under pressure in the presence of iron catalysts to the corresponding alcohols. It was also interesting to study under the same conditions the reduction of benzaldehyde and of aromatic ketones containing a carbonyl group in the side chain. This investigation was deemed necessary since aromatic aldehydes and ketones [1] are readily hydrogenated into naphthenes in the presence of nickel oxide. For example, 1,4-dihydroxy-1,4-dimethylbenzene (C_6H_4—$(CH_2OH)_2$) sent to me through the kindness of Professor Bischoff was converted completely into para-dimethylcyclohexane in the presence of nickel oxide in spite of the fact that the lowest possible temperature for hydrogenation was employed. Before discussing the hydrogenation of benzyl alcohol it is advisable for the better understanding of the reaction to first describe an experiment on the hydrogenation of benzaldehyde.

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[1] Ipatieff, Ber., *41*, 993 (1908).

[2] Ipatieff, Ber., *40*, 1270 (1907).

Forty grams of benzaldehyde was heated in the high pressure apparatus in the presence of an iron catalyst under an initial hydrogen pressure of 100 atmospheres for 12 hours at 280°, or until no further decrease in pressure was observed. The product of the reaction was a mixture of water, a liquid which on distillation was found to be toluene, a small amount of unchanged benzaldehyde, a considerable amount of hydrocarbon boiling at 280–290° (dibenzyl), and a small amount of condensation product.

Anal. Calcd. for $C_{14}H_{14}$: C, 92.3; H, 7.7. Found: C, 92.4; H, 7.8.

According to these results, it is assumed that benzaldehyde is first hydrogenated to *benzyl alcohol,* some of which is further reduced to toluene and some of which is dehydrated to dibenzyl ether, the latter being converted into dibenzyl in the presence of hydrogen and perhaps partly into toluene.

$$C_6H_5CHO + H_2 \rightarrow C_6H_5CH_2OH$$

$$C_6H_5CH_2OH + C_2H_5CH_2OH \rightarrow H_2O + C_6H_5CH_2OCH_2C_6H_5$$

$$C_6H_5CH_2OCH_2C_6H_5 + H_2 \rightarrow H_2O + C_6H_5CH_2CH_2C_6H_5$$

The experimental results obtained with benzaldehyde were in complete agreement with those on the hydrogenation of benzyl alcohol under pressure in the presence of iron, thus confirming the correctness of the equations written for the latter reaction.

Forty grams of benzyl alcohol was heated 6 hours at 350–360°

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[1] Ipatieff, Ber., *40*, 1286 (1907).

in an iron tube in the high pressure apparatus, the initial pressure being 96 atmospheres. After cooling, the pressure in the apparatus was 40 atmospheres. The reaction product consisted of 8 g. of water and 37 g. of liquid distilling at 110–310°. The first fraction (14 g.) boiled at 110–130° and consisted chiefly of toluene; the second fraction (11 g.) boiled at 130–270° and contained *benzyl alcohol, benzaldehyde,* and *dibenzyl;* the third fraction, boiling at 270–310°, and solidifying to a crystalline mass, was pure dibenzyl.

Anal. Calcd. for $C_{14}H_{14}$: C, 92.3; H, 7.7. Found: C, 92.2; H, 7.7.

Thus, the formation of dibenzyl from benzyl alcohol in the presence of hydrogen was confirmed. The experiments on the action of hydrogen upon benzyl alcohol and benzaldehyde in the absence of the iron catalyst also led to the same conclusion. When the hydrogenation of benzaldehyde was made in the high pressure apparatus in a *copper tube* at 310–315° no formation of dibenzyl was observed. As previously indicated,[1] benzaldehyde is not reduced to benzyl alcohol by hydrogen in a copper tube under high pressure; therefore it is understandable why dibenzyl cannot be formed under these conditions. When benzyl alcohol was placed in the high pressure apparatus in a copper tube, the alcohol was reduced at 400° in the presence of hydrogen, partly to toluene and partly to dibenzyl. Analysis of the higher boiling hydrocarbon indicated that it was *dibenzyl.*

Anal. Calcd. for $C_{14}H_{14}$: C, 92.3; H, 7.7. Found: C, 92.9; H, 7.9.

But it should be noted that because of the higher temperature, there was more tar formed and the yield of dibenzyl was smaller than when using an iron tube.

When benzyl alcohol was heated in the high pressure apparatus in an iron tube at 400°, without hydrogen, it decomposed into benzaldehyde and hydrogen, as already shown in earlier experiments. The benzaldehyde decomposed further, into carbon monoxide and benzene, and the hydrogen which was liberated acted upon the benzyl alcohol, hydrogenating it partly into toluene and partly into dibenzyl.

All these experiments lead to the conclusion that the formation of dibenzyl from benzaldehyde results from the hydrogenation of benzaldehyde to benzyl alcohol, which on further reaction with hydrogen, is hydrogenated partly to toluene and partly to dibenzyl.

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[1] Ipatieff, Chem. Zentr., 1906, II, 86.

Hydrogenation of Triphenyl Carbinol and Phenylfluoryl Carbinol.[1]—Theoretically, it would be expected that the hydrogenation of triphenyl carbinol would proceed in four phases: (1) separation of water and the formation of triphenylmethane; (2) hydrogenation to diphenylcyclohexylmethane; (3) formation of phenyldicyclohexylmethane; (4) formation of a product corresponding to complete hydrogenation, namely, tricyclohexylmethane.

In the literature there is a description of the experiments of Godchot[2] who first obtained tricyclohexylmethane by the reduction of triphenylmethane according to the method of Sabatier and Senderens. Godchot's product was an oil of aromatic odor; b.p., 140° at 20 mm.; d_{20}, 0.8406. When this substance was treated with concentrated sulphuric acid, a dark brown color appeared which indicated that the product was not completely hydrogenated. Godchot did not mention in his paper whether or not his product reacted with nitrating mixture. It would be expected that tricyclohexylmethane would be very stable towards nitrating mixture and inert in general and these expectations were experimentally confirmed. It is therefore to be concluded that Godchot was not dealing with tricyclohexylmethane.

Preliminary experiments showed that at 230° a separation of water from triphenyl carbinol occurred with formation of tricyclohexylmethane. The optimum temperature for hydrogenation was 275°. Below this temperature the reaction was incomplete. At 300° a decomposition took place and theoretical yields of tricyclohexylmethane could not be obtained; consequently, the main course of the reaction is as follows:

$$(C_6H_5)_3COH + 10H_2 \rightarrow (C_6H_{11})_3CH + H_2O$$

but secondary reactions proceed simultaneously, and in two directions,

$$\text{(I)}\quad (C_6H_5)_3COH + 11H_2 \rightarrow (C_6H_{11})_2CH_2 + C_6H_{12} + H_2O$$

$$\text{(II)}\quad (C_6H_5)_3COH + 11H_2 \rightarrow C_6H_{11}C_6H_{11} + C_6H_{11}CH_3 + H_2O$$

The formation of dicyclohexylmethane proceeds much more readily than the formation of dicyclohexyl; that is to say, the first reaction is the more important of the two. The amount of decomposition, the yield of dicyclohexylmethane, and the formation of cyclohexane increased with rise in temperature. At 300°, the reaction which is predominant at lower temperatures (the formation of tricyclohexylmethane) hardly takes place at all. The products formed at 300° are liquids containing dicyclohexylmethane. A more profound decomposition of the molecule also takes place as evidenced by the formation of methane, but only to a small extent.

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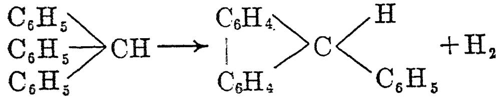
[1] This work was carried out together with Dolgoff. Ipatieff and Dolgoff, Bull. soc. chim., *39*, 1456 (1926).

[2] Godchot, Compt. rend., *147*, 1057 (1908); Bull. soc. chim., (4) 7, 958 (1910).

A detailed study of the hydrogenation products of triphenyl carbinol showed the formation of tricyclohexylmethane under the hydrogenating conditions used, but this hydrocarbon was markedly different in chemical and physical properties from the hydrocarbon obtained by Godchot.

As triphenylmethane may be converted, in certain cases, into phenylfluorene at a temperature of about 300°,



it is doubtful whether the hydrocarbon obtained by us was the final hydrogenation product of phenylfluorene (perhydrophenylfluorene). In order to solve this question, phenylfluorylcarbinol was synthesized and then hydrogenated. The resulting product was quite different in its properties; it was perhydrophenylfluorene. We therefore assume that *tricyclohexylmethane* was actually obtained by the hydrogenation of triphenyl carbinol.

The alcohol used for the above experiment was prepared by means of the Grignard reaction, starting with C_6H_5MgBr and $C_6H_5COC_6H_5$. The hydrogenation was made in the high pressure apparatus, in which 25 g. of triphenyl carbinol dissolved in 50 g. of cyclohexane was placed in the presence of a nickel oxide catalyst. An initial pressure of 80–100 atmospheres of hydrogen was used and a temperature of 275°. When the supply of hydrogen diminished, the apparatus was cooled and a fresh supply was added. The reaction product was poured into a graduate to measure the water formed and after removing the catalyst by filtration and the solvent by distillation, the product remaining was a colorless liquid giving no reaction with nitrating mixture and distilling into two fractions: (1) 220–300°; (2) 330–335°. The first fraction was a mobile liquid; the second, a sirupy liquid which solidified to a white crystalline mass on standing. The first fraction was redistilled to produce three fractions: (1) 242–246°; (2) 250–253°; (3) 255–258°. The first fraction had the following constants: n_D^{22}, 1.4767; d_0^{25}, 0.8619.

It was *dicyclohexyl*, its constants being identical with those obtained by Ipatieff, Wallach, and Eijkman.[1]

Anal. Calcd. for $C_{12}H_{22}$: C, 86.6; H, 13.4. Found: C, 86.5; H, 13.3.

The second and third fractions (b.p., 250–253° and 255–258°) showed similar constants and analytical figures; n_D^{23}, 1.4749; M_D, 58.05; d_0^{20}, 0.8755. This product was *dicyclohexylmethane.*

Anal. Calcd. for $C_{13}H_{24}$: C, 86.3; H, 13.4. Found: C, 85.6; H, 13.6.

The lower and higher boiling fractions were not analyzed. In all probability the fraction boiling at 225–240° contained considerable dicyclohexyl and in the higher boiling fraction, perhydrofluorene was present.

All fractions were insoluble in water and difficultly soluble in cold alcohol (0.2–0.25 cc. in 6–10 cc. alcohol) and in glacial acetic acid, but they were readily soluble in ether, benzene, and cyclohexane. When heated with sulphuric acid, no coloration was observed. (A barely perceptible yellow coloration appeared on long standing.) These substances did not react with nitrating mixture, nor with a solution of potassium permanganate, nor with bromine.

The crystalline mass which separated from the liquid product was recrystallized several times from alcohol. The crystals were prismatic in shape, had the appearance of snow-white cotton, melting at 47.5°, and boiling at 320–326°. They were insoluble in water, very slightly soluble in alcohol in the cold and in glacial acetic acid, but readily soluble in ether, benzene, and cyclohexane. This crystalline material was not affected by nitrating mixture, did not react with a solution of potassium permanganate, and it was not changed by the action of 20% sulphuric acid nor a solution of chromic-acetic acid. Thus, this product was very stable and, according to its constants, it was assumed to be *tricyclohexylmethane.*

Anal. Calcd. for $C_{19}H_{34}$: C, 87.0; H, 13.0; mol. wt., 262; M.R.,

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[1] Ipatieff, Chem. Zentr., 1907, II, p. 203; Wallach, *ibid.*, 1904, I, 763; Eijkman, Chem. Weekblad, *1*, 7 (1903).

83.25. Found: C, 87.8, 87.0; H, 13.0, 13.0; mol. wt., 265; M.R., 82.97; n_D^{50}, 1.4985; d_0^{50}, 0.9282.

Hydrogenation of Phenylfluoryl Carbinol.—This alcohol, prepared according to the method of Ullmann and Würstenberger,[1] was subjected to hydrogenation under conditions similar to those used with triphenyl carbinol, and also in the presence of cyclohexane as solvent. In the first hydrogenation (at 275°) the reaction did not proceed to completion as shown by the fact that the product reacted with nitrating mixture. The second hydrogenation was made at 300°, but at this temperature the product suffered partial decomposition into cyclohexane and perhydrofluorene. On distillation, the main fraction came over at 326–336° and solidified readily to a white crystalline mass which resembled in appearance the crystalline product obtained in the hydrogenation of triphenyl carbinol. The material was readily soluble in ether, benzene, and cyclohexane, and after three recrystallizations from alcohol it was obtained as thin needles melting at 53°. Neither bromine nor nitrating mixture had any effect upon this substance, but when it was heated with sulphuric acid a slight yellow coloration was obtained.

Anal. Calcd. for $C_{13}H_{32}$: C, 87.6; H, 12.4; Found: C, 87.5; H, 12.4; n_D^{50}, 1.4919; d_0^{50}, 0.9418.

The above data justifies the conclusion that this hydrogenation product was *perhydrophenylfluorene*. However, if a comparison of the properties of the products obtained by the hydrogenation of both alcohols is made an essential difference is seen.

HYDROGENATION OF

$(C_6H_5)_3COH$	$(C_6H_4)_2 = COH$
1. Carried out at 275°; at 300°, decomposition begins.	1. Does not hydrogenate completely at 275°; complete reduction occurs at 300°.
2. Yield, 40–45%.	2. Yield, 80–90%.
3. 30–45% decomposition products	3. 10% decomposition products.
4. Melting point, 47.5°.	4. Melting point, 53.0°.
5. Boiling point, 320–326°.	5. Boiling point, 326–336°.
6. $d_0^{50} = 0.9286$, $n^{50} = 1.4985$, M.R. = 82.97, Mol. wt. = 264.8.	6. $d_0^{50} = 0.9413$, $n_D^{50} = 1.4919$, M.R. = 80.13, Mol. wt. = 261.1.

The products of the hydrogenation of triphenyl carbinol and of phenylfluoryl carbinol were tricyclohexylmethane and perhydrophenylfluorene, respectively, the latter being a new compound.

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[1] Ullmann and Würstenberger, Ber., 37, 73 (1904).

Hydrogenation of para-Hydroxytetraphenylmethane.—This compound was synthesized according to the method of Baeyer and Villiger[1] by the condensation of triphenyl carbinol with phenol by means of concentrated sulphuric acid. The product was obtained as small needles melting at 281° [$HOC_6H_4(C_6H_5)_3C$]. Hydrogenation was carried out in two steps under the same conditions as for tetraphenylmethane. The first hydrogenation produced phenyldicyclohexylmethane; the second, tricyclohexylmethane.

After the removal of cyclohexane, a liquid was obtained which possessed, when heated, an agreeable rose odor. It was separated into three fractions: (1) boiling at 146–148° (760 mm.); (2) 122–125° (17 mm.); (3) 196–197° (17 mm.).

From the *first fraction,* cyclohexanol (b.p., 154–162°) was separated by distillation. After heating with phenylisocyanate for 1 hour and diluting with ligroin, a white crystalline substance melting at 80° was obtained. This substance was identified as cyclohexanolphenylurethane; the melting point of a mixture of this substance with the urethane prepared from cyclohexanol, was also 80°.

Anal. Calcd. for $C_{13}H_{17}O_2N$: C, 71.2; H, 7.7; N, 6.4. Found: C, 72.0; H, 7.4; N, 7.2; N_D^{20}, 1.4460.

The *second fraction* (b.p., 122–125°) was *dicyclohexylmethane,* having following constants: d_{20}^{20}, 0.8851; d_0^{20}, 0.8829; n_D^{20}, 1.4786; M.R., 57.83.

Anal. Calcd. for $C_{13}H_{24}$: C, 86.6; H, 13.4. Found: C, 86.7; H, 12.9.

The *third fraction* boiling at 196–197°, showed the following constants: d_0^{20}, 0.9737; d_{20}^{20}, 0.9671; d_{20}^{50}, 0.9550; n_D^{20}, 1.5258.

Anal. Calcd. for C_nH_{2n-6}: C, 88.8; H, 11.2; M.R., 80.7. Found: C, 88.6; H, 11.4; M.R., 80.7.

The third fraction was again hydrogenated. After hydrogenation for three days at 275°, and after distilling off the cyclohexane, an oil was obtained which solidified on cooling. The solid material after recrystallization from methyl alcohol gave the following constants: m.p., 48°; b.p., 322–329° (750 mm.); n_D^{20}, 1.4865; d_0^{50}, 0.9263. The hydrogenation product obtained from parahydroxytetraphenylmethane was doubtless *tricyclohexylmethane.*

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[1] Baeyer and Villiger, Ber., *35*, 3018 (1902).

Anal. Calcd. for $C_{19}H_{34}$: C, 7.0; H, 13.0; mol. wt., 262. Found: C, 87.2; H, 13.0; mol. wt., 262 (benzene).

Hydrogenation of para-Oxytriphenyl Carbinol $[HOC_6H_4(C_6$ $COH]$ *and para-Oxydiphenyl Carbinol* $[HOC_6H_4(C_6H_5)CHOH]$.[1] The above results on the hydrogenation of para-oxytetraphenylmethane under pressure made it desirable to study the hydrogenation of para-oxytriphenyl carbinol. The same tricyclohexylmethane was obtained from this substance as from triphenyl carbinol and para-oxytetraphenylmethane in spite of the fact that the starting material had an hydroxyl group present in the aromatic nucleus. The phenolic hydroxyl group was split off under the conditions of the experiment which is in agreement with facts previously discovered.

The difference in chemical properties of the hydroxyl derivatives of the phenols and tertiary alcohols is known. In triphenyl carbinol, the greater part of the affinity of the central carbon atom is saturated by three phenyl radicals and to this is due the extreme mobility of the hydroxyl group which is bound to the same carbon atom.

The reactions of triphenyl carbinol were studied by A. v. Baeyer who showed that the hydroxyl group of this substance possesses the function of an aldehyde, in that it is capable of combining with sodium bisulphite, hydroxylamine, phenylhydrazine, etc. It is to be understood that such affinity of the hydroxyl group of the triphenyl carbinol leads to saturation by hydrogen during hydrogenation, and because of this, both triphenylmethane and tricyclohexylmethane are obtained. The phenolic hydroxyl group does not possess such mobility, and therefore, it cannot be removed during hydrogenation. In order to hydrogenate it, a higher temperature is necessary. Hydrogenation experiments by Sabatier and Senderens [2] showed that at 250–300° benzene is obtained from phenol. Ipatieff and Orloff [3] also found that at a temperature around 310°, hydroxydicyclohexylmethane is converted into dicyclohexylmethane.

A preliminary hydrogenation study of para-hydroxytriphenyl carbinol showed that at 220° under a hydrogen pressure of 100–150 atmospheres, water separates and the formation of parahydroxytriphenylmethane (first phase of hydrogenation) takes place. This first phase of the reaction might be represented as follows, and in agreement with Gomberg,[1] the carbinol has the quinone structure.

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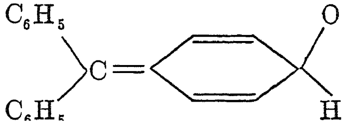
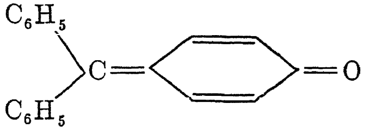
[1] Ipatieff and Dolgoff, Bull. soc. chim., *43*, 242 (1928).
[2] Sabatier and Senderens, Ann. [8], *4*, 371 (1905).
[3] Ipatieff and Orloff, Bull. soc. chim., [4], *41*, 208 (1926).

(I)



At 300°, 50% of the carbinol is converted into fuchsone (diphenylquinonemethane). It was first obtained and described by Bystrycki and Herbst.[2]

(II)

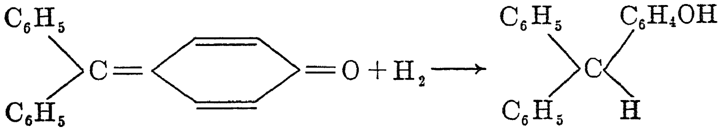


Fuchsone and the carbinol give, according to the opinion of these writers, a double compound:

$$(C_6H_5)_2C{=}C_6H_4{=}O + HOC_6H_4(C_6H_5)_2COH \rightarrow C_{38}H_{30}O_3$$

According to Baeyer,[3] the first compound is of the quinhydrone type which is unstable and at 200° is converted completely into fuchsone.

According to the works of Bystrycki and Herbst, fuchsone is reduced to para-hydroxytriphenylmethane:



Our investigation showed that para-hydroxytriphenylmethane decomposes partially (up to 40%) at about 220–230° giving phenol and diphenylmethane.

$$- H_2 \rightarrow C_6H_5OH + C_6H_5{-}CH_2{-}C_6H_5$$

When the hydrogenation is conducted at 270°, cyclohexanol, dicyclohexylmethane, and tricyclohexylmethane are obtained. It is interesting to note that hydrogenation at this temperature quantitatively converts para-hydroxytriphenylmethane into tricyclohexylmethane, the hydroxyl group being eliminated. This same phenomenon was observed with para-hydroxydiphenylmethane as described below.

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[1] Gomberg, Chem. Soc., *35*, 1036 (1913).

[2] Bystrycki and Herbst, Ber., *36*, 3568 (1903).

[3] Baeyer, Ber., *36*, 2798 (1903).

The carbinol decomposes further at 320°, being reduced to hydrocarbon. Only 10–12% of the starting material remained unchanged. Among the decomposition products were cyclohexane, dicyclohexylmethane, tricyclohexylmethane; only a trace of cyclohexanol was found. Para-hydroxytriphenyl carbinol is much less stable than triphenyl carbinol, which does not decompose even at 220°. The cause of this instability must be ascribed to the phenolic hydroxyl group which donates high mobility to the hydroxyl group on the central carbon atom. However, the yield of tricyclohexylmethane was not large, only about 25–30%, although under similar conditions the yield from triphenyl carbinol was as high as 50%. Part of the carbinol was polymerized to tar. Our experiments with para-hydroxytriphenylacetic acid showed that elimination of carbon dioxide takes place during hydrogenation and that after conversion into para-hydroxytriphenylmethane another hydrogenation occurs, as described above, which confirms the results of the experiments conducted by Jaeger and Berger [1] who obtained triphenylmethane and triphenyl carbinol by catalysis and photolysis starting with the sodium salt of triphenylacetic acid.

We were able to eliminate the phenolic hydroxyl group in a series of experiments with para-hydroxydiphenylmethane. The sole product of the hydrogenation at 260° was dicyclohexylmethane, the hydroxyl group being removed to form water.

The para-hydroxytriphenyl carbinol used in these experiments was obtained synthetically according to the method of Bystrycki and Herbst [2] by the reaction of sulphuric acid upon para-hydroxytriphenylacetic acid. This reaction resulted in the formation of orange crystals melting at 132°. Experiments on the hydrogenation of this carbinol were made in the high pressure apparatus using a solution of the carbinol in cyclohexane in the presence of nickel oxide under an initial hydrogen pressure of 80–100 atmospheres. On hydrogenation at 230°, 25 g. of product was obtained and 16 atmospheres of hydrogen was consumed (the capacity of the bomb was 800 cc.). The hydrogenated product consisted of a liquid with a yellowish coloration and water. After distilling off the cyclohexane, the following fractions were obtained: (1) 160–210°

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[1] Jaeger and Berger, Chem. Soc., *119*, 2070 (1921).

[2] Bystrycki and Herbst, Ber., *34*, 3474 (1901).

(odor of phenol); (2) 250–265° (odor of diphenylmethane); (3) chief fraction.

The fractions boiling at 160–210° and at 250–265° were combined and treated with sodium hydroxide. The oil which did not react with the alkali was separated. It distilled without residue at 260–263° and was *diphenylmethane.*

The phenol, separated in the usual way, distilled at 181–183°. It gave the reactions characteristic of phenol and solidified to a crystalline mass upon the addition of a small crystal of phenol.

The third fraction, a thick tarry liquid, constituting about 70% of the total amount of carbinol, was distilled under a pressure of 25 mm. It gave the following fractions: (1) 139–145° (the remainder of the diphenylmethane); (2) 250–253° (a thick, yellowish oil, resembling honey).

The fraction boiling at 250–253°, after treatment with petroleum ether, solidified to a white crystalline mass which after recrystallization from a mixture of benzene and petroleum ether, melted at 107–108°. This substance was *para-hydroxytriphenylmethane,* described by Bystrycki and Herbst; [1] they also obtained fuchsone.[2]

Anal. Calcd. for $C_{19}H_{16}O$: C, 87.8; H, 6.3; O, 6.3. Found: C, 87.8; H, 6.2; O, 6.1.

Para-hydroxytriphenylmethane was hydrogenated at 270–275°. An oil distilling at 320–330° was obtained which crystallized after standing for three days. Recrystallization from alcohol gave crystals which had the following properties: m.p., 48°; d_0^{50}, 0.9265; n_D^{60}, 1.4976.

Anal. Calcd. for $C_{19}H_{34}$: C, 87.0; H, 13.0; mol. wt., 262. Found: C, 86.9; H, 13.0; mol. wt., 245.

The yield of tricyclohexylmethane was in some cases as high as 90% of the theoretical amount. Under similar hydrogenation conditions at 280° and starting with para-hydroxytriphenyl carbinol, a transparent, colorless oil was obtained which gave the following fractions on distillation: (1) 140–170°; (2) 240–270°; (3) 320–335°.

From the first fraction (b.p., 140–170°) cyclohexanol was isolated (b.p., 164–168°). It was identified through its phenylurethane, m.p., 81°; n_D^{22}, 1.4643 (C, 71.8; H, 12.1).

The fraction boiling at 270–280°, after treatment with concentrated sulphuric acid followed by distillation over sodium, gave a fraction (b.p., 249–254°; n_D^{22}, 1.4752; d_{20}^{20}, 0.8776), corresponding to *dicyclohexylmethane.*

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[1] *Ibid.*, *35*, 3137 (1902).

[2] *Ibid.*, *36*, 2337, 3505 (1903).

Anal. Calcd. for $C_{13}H_{24}$: C, 86.5; H, 13.4. Found: C, 86.6; H, 13.2.

The fraction boiling at 320–330° was a thick oil, which reacted with nitrating mixture. Therefore, it was subjected to a second hydrogenation. The product boiled at 280° and solidified on cooling. It was crystallized from alcohol and after drying it consisted of white crystals possessing the properties of *tricyclohexylmethane.*

In conducting the hydrogenation of para-hydroxytriphenyl carbinol at 320°, an increase was observed in the yield of cyclohexane as well as of the gaseous saturated hydrocarbons, such as methane, etc. Distillation of the product yielded chiefly dicyclohexylmethane together with a small amount of tricyclohexylmethane, the latter suffering decomposition under these conditions. Analyses of the hydrocarbons obtained proved their composition.

It should be noted that the crystalline substance melting at 47–48° obtained in this and preceding experiments was identical with the tricyclohexylmethane obtained by Zamenski and Saverdowski.[1]

Hydrogenation of para-Hydroxytriphenylacetic Acid [HOC_6H_4-$(C_6H_5)_2CCOOH$].—The starting material was obtained by the synthetic method of Bystrycki and Herbst [2] from phenol and hydroxyphenylacetic acid in benzene solution in the presence of stannous chloride. The product consisted of yellow crystals, melting at 211°. Hydrogenation gave carbon dioxide, methane, cyclohexanol, dicyclohexylmethane, and tricyclohexylmethane. The first stage of the hydrogenation consisted in the elimination of carbon dioxide, the second stage being the hydrogenation of the para-hydroxytriphenylmethane thus formed.

Hydrogenation of para-Hydroxydiphenylmethane.—This compound was synthesized according to the method of Paterno [3] and Zinke.[4] The product had the appearance of silky threads and melted at 83°. Its hydrogenation was carried out at 250–260° with an initial hydrogen pressure of 100 atmospheres. After cyclohexane was distilled from the product, a small amount of water and a colorless, transparent oil remained which distilled almost completely within a temperature range of 4–5°. When this substance was heated with metallic sodium only traces of hydrogen were obtained which indicated that it did not contain the hydroxyl group. After washing the oil with concentrated sulphuric acid and redistilling it over sodium the boiling point was 250–254°. Further evidence that it was *dicyclohexylmethane* was furnished by its analysis and properties.

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[1] Zamenski and Saverdowski, Ber., *60*, 713 (1927).

[2] Bystrycki and Herbst, Ber., *34*, 3064 (1901).

[3] Paterno, Gazz. chim. ital., *2*, 2 (1872).

[4] Zinke, Ann., *334*, 373 (1904).

Anal. Calcd. for $C_{13}H_{24}$: C, 86.5; H, 13.4. Found: C, 86.6; H, 13.3.

The oil was completely inert toward various reagents. For conclusive proof of its structure, it was subjected to dehydrogenation according to the method of Ruzicki, namely, 3 g. of the oil and 3.2 g. of flowers of sulphur were heated at 280° for six hours. The product of the reaction was extracted with ether and after distilling off the latter, a substance possessing the properties of *diphenylmethane* was separated.

CONCLUSIONS

(1) In the first phase of hydrogenation, para-hydroxytriphenyl carbinol is converted into para-oxytriphenylmethane, passing through fuchsone.

(2) Fifty per cent of the para-hydroxytriphenylmethane decomposes into phenol and diphenylmethane at 220° and 100 atmospheres of hydrogen pressure.

(3) The para-hydroxytriphenylmethane which does not decompose is hydrogenated almost quantitatively at 270–280°.

(4) During hydrogenation, para-hydroxydiphenylacetic acid loses carbon dioxide and is converted into para-hydroxytriphenylmethane.

(5) At 260° para-oxydiphenylmethane is hydrogenated quantitatively to dicyclohexylmethane.

(6) The phenolic hydroxyl group is split off during hydrogenation under pressure at 260–280°; the tertiary alcoholic hydroxyl group is split off at 200–220°.

HYDROGENATION OF β-HYDROXYDINAPHTHYLPHENYLMETHANE AND DIPHENYL-ALPHA-NAPHTHYL CARBINOL [1]

In the preceding pages it was shown that hydrogenation of the derivatives of triphenylmethane under pressure is accompanied by the partial decomposition of its molecule with the formation of hydrogenated derivatives of triphenylmethane. The hydroxyl group of phenol, if present, splits off during hydrogenation.

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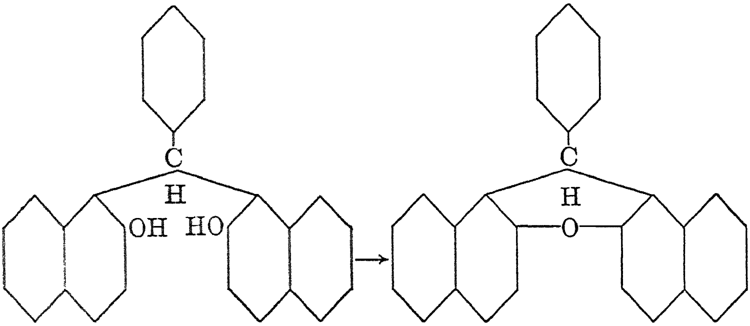
[1] Ipatieff and Dolgoff, "On the Rupture of some Derivatives of Naphthyl Methanes during Hydrogenation under Pressure," Bull. soc. chim., *45*, 950 (1920).

The following investigation deals with certain derivatives of naphthyl methane, the purpose being to determine the ability of the naphthyl and phenyl radicals to resist removal from the molecule and also to answer certain questions concerning the hydrogenation of xanthenes, a field scarcely touched by experimentation.

The first of these substances to be studied were beta-beta-dihydroxydinaphthylmethane and beta-beta-dihydroxydinaphthylphenylmethane, both of which were readily obtainable. These substances were chosen with the idea of determining the mechanism of their conversion to the corresponding xanthenes. It is known from the literature that many such derivatives containing two hydroxyl groups are able to split out a molecule of water and be converted into xanthenes, a reaction involving the formation of a ring through oxygen. This reaction takes place only when the hydroxyl groups are present in the ortho position; meta- and para-isomers do not give xanthenes.



The formation of xanthenes in the series of derivatives of triphenyl and naphthylphenylmethane has been investigated by several workers.[1] Kaufmann and Egner noticed that the presence of the naphthalene nucleus facilitated the formation of xanthenes. This formation sometimes occurs with such ease that special care must be taken to prevent the carbinol from being converted completely into xanthene.

Claisen [2] showed that beta-beta-dihydroxynaphthylphenylmethane is quite unstable and that when heated in glacial acetic acid it yields xanthene.

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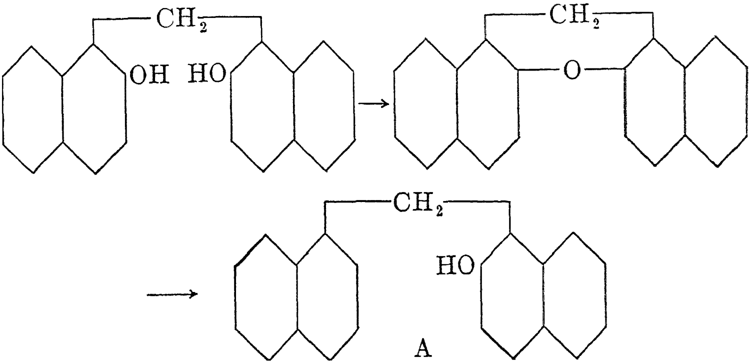
[1] Beager, Ann., *354*, 108 (1907); Fosse, Compt. rend., *133*, 100 (1901); Kaufmann and Egner, Ber., *46*, 3779 (1913).

[2] Claisen, Ann., *257*, 261 (1890).

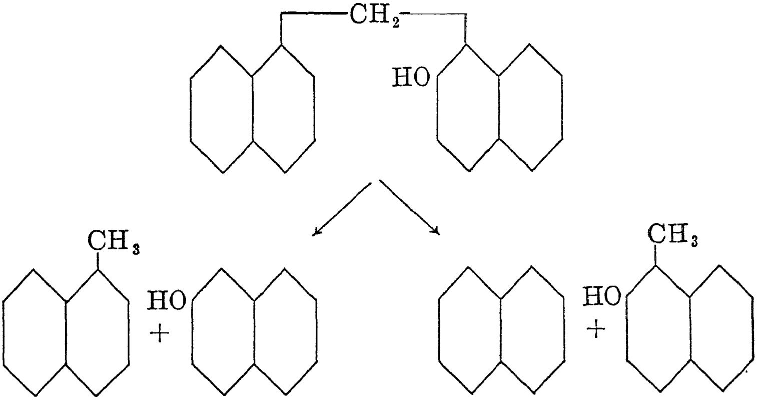
According to Wolff,[1] beta-beta-dihydroxydinaphthylphenylmethane is converted into xanthene by heating it in toluene solution at 110° in the presence of sulphuryl chloride. Obviously, in this case, the reaction proceeds with some difficulty.

On the basis of the present investigation on beta-beta-dihydroxydinaphthylmethane it may be concluded that the xanthene formed during the reaction decomposes completely during further hydrogenation according to the following scheme.



A

Phenol A decomposes in two directions, depending upon the location of the rupture:



The following substances were isolated: naphthalenes of various degrees of hydrogenation (chiefly decalin, traces of tetralin), dihydro beta-naphthol, and a small amount of xanthene in the form of its tetrahydro derivatives. Besides these, a large amount of condensation products and tarry materials was obtained. In all probability, the latter may have an internal bond through oxygen. It consisted of a complex mixture of substances which could not be separated by distillation.

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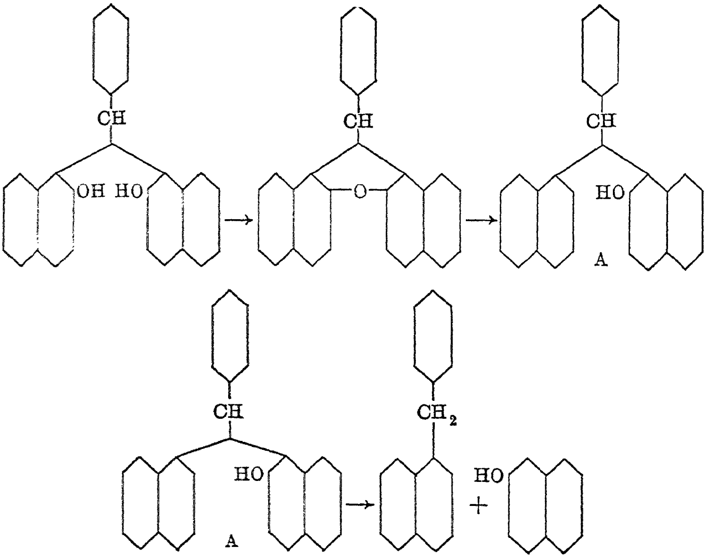
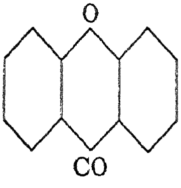
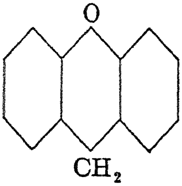
[1] Wolff, Ber., *26*, 84 (1893).

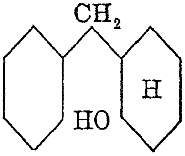
In the case of beta-beta-dihydroxydinaphthylphenylmethane, the process occurred in a similar manner.



In both cases we succeeded in isolating the intermediate phenol. In all probability it is unstable under the conditions of the reaction and decomposes according to the scheme proposed.[1] The presence of a phenol of similar structure was proven also in the work of Ipatieff and Orloff.[2]







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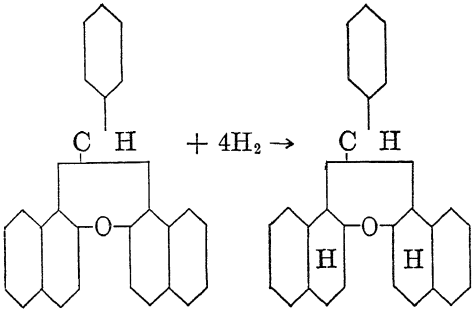
[1] H in the ring means that this ring was hydrogenated.

[2] Ipatieff and Orloff, Bull. soc. chim., (4), *41*, 208 (1927).

The starting material, xanthone, is converted by hydrogen into xanthene which then ruptures to give a substituted phenol. The scission of the molecule occurs partly to give benzyl naphthalene and beta-naphthol but more in the direction to produce naphthalene and benzyl beta-naphthol. However, we succeeded in isolating naphthalenes of various degrees of hydrogenation, namely, beta-deca-hydronaphthol, the derivative of the hydrogenation of benzylnaphthalene and probably ditetralinphenylxanthene, a product of the hydrogenation of beta-beta-dioxynaphthylmethane.



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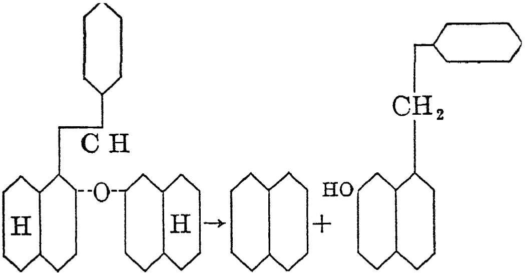
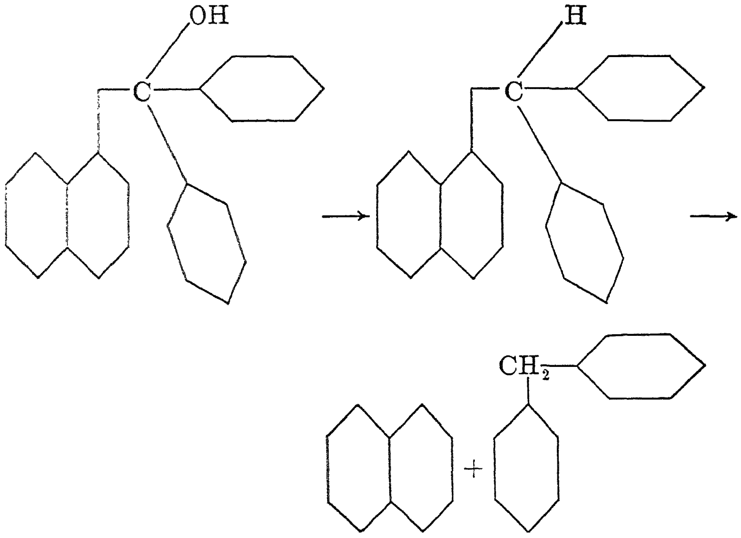


It is impossible to obtain perhydroxanthene. Obviously, under the conditions of the experiment, an equilibrium is established in the distribution of the hydrogen atoms between the naphthalene and the benzene *nuclei*. To be sure, intensive hydrogenation ruptures the xanthene molecule and substances such as those described below are formed, as well as tarry products. The latter are always formed, and in considerable amount. In their properties they are similar to the products obtained in the hydrogenation of dihydroxynaphthylmethane.

In the reactions described, the benzene nucleus is very stable. We were not successful in isolating even a trace of cyclohexane, the entire product obtained by this reaction retaining the phenyl groups unchanged.

Diphenyl-alpha-naphthyl carbinol was used in this experiment in order to study the decomposition of a substance which possesses the nuclei of benzene and naphthalene and at the same time is incapable of forming xanthenes. During hydrogenation almost complete decomposition took place according to the following scheme:



The bonds between the central carbon atom and the benzene nucleus are more stable than those between this carbon atom and the naphthalene nucleus. The instability of this union is revealed by the rupture of the molecule. The hydroxyl group was first substituted by hydrogen, forming diphenyl-alpha-naphthylmethane. This latter, during hydrogenation, decomposed further with the formation of hydrogenated naphthalenes and dicyclohexylmethane. After these hydrogenated hydrocarbons were distilled from the reaction mixture, a dark colored, rubber-like residue remained which could be distilled under diminished pressure to produce a transparent, colorless product which became a glass-like mass when cold.

The beta-beta-dihydroxydinaphthylmethane used in the experiments was synthesized according to the method of Abel [1] and Wolff,[2] which consists in the condensation of beta-naphthol with formaldehyde by gently heating in a 50% acetic acid solution or in dilute alcohol. It was necessary to keep the temperature of the bath below 70° because otherwise the product assumed a dark purple color and during crystallization a large amount of it was lost. After separation of the crystals, the acetic acid filtrate could be used in subsequent condensations. Upon recrystallization from alcohol, silky needles were obtained which melted at 192–193°.

One hundred grams of the substance was subjected to hydrogenation in two portions. The hydrogenation was carried out in 800 cc. high pressure apparatus in which was placed 50 g. beta-beta-dihydroxynaphthylmethane dissolved in 100 g. of cyclohexane together with 5–8 g. of nickel oxide. The initial pressure of hydrogen was 80–100 atmospheres and the hydrogenation temperature was 250–260°.

At the end of the hydrogenation reaction the gas contained a small quantity of paraffinic hydrocarbons. The solvent was distilled from the reaction product, leaving a green fluorescent oil which was distilled with steam. Redistillation gave 55 g. of a colorless oil which became yellow on exposure to air, while 37 g. of a dark colored, rubber-like mass remained in the distillation flask. The oil which distilled was separated into three fractions: (1) 185–215° (32 g.); (2) 215–245° (4 g.); (3) greater than 245° (5 g.).

The first fraction which had the odor of tetralin was hydrogenated at 270° yielding a colorless oil which, after washing with sulphuric acid and water and drying, distilled at 187–196°. Redistillation yielded a colorless fraction with the properties of decalin: b.p., 188–191°; d^{15}_{15}, 0.8765; n^{15}_{D}, 1.4358.

Anal. Calcd. for $C_{10}H_{18}$: C, 87.0; H, 13.0; mol. wt., 138. Found: C, 86.9; H, 13.2; mol. wt., 142.

Five grams of this product was dehydrogenated at 210–230° with 2 g. of flowers of sulphur; the product was naphthalene.

The second fraction (b.p., 215–245°) was an oil which became colored on standing in the air. Heating this oil with phenylisocyanate produced a crystalline substance which, after recrystallization from alcohol, melted at 164°.

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[1] Abel, Ber., *25*, 3478 (1892).

[2] Wolff, Ber., *26*, 84 (1893).

Anal. Calcd. for $C_{17}H_{23}O_2N$: N, 5.1. Found: N, 5.0.

According to these data, this crystalline substance was the phenylurethane of decahydronaphthol. During the distillation of the fraction boiling at 215–245°, a fraction boiling at 225–240° was separated which crystallized on standing. This substance after recrystallization from alcohol melted at 74°.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.4; H, 12.3. Found: C, 77.2; H, 12.3.

Therefore, this substance was beta-decahydronaphthol. The data obtained were in complete agreement with those of Leroux [1] and also with mine.[2]

The oil remaining after separation of the crystals, and the fraction boiling at 240–270°, were not subjected to detailed investigations because the hydroxyl group was found to be present. In all probability they represent a mixture of naphthols of various degrees of hydrogenation.

The rubber-like substance remaining in the flask and not volatile with steam was distilled under diminished pressure (18 mm.) to give three fractions: (1) 133–145°; (2) 230–245°; (3) 255–270°. However, the greater part of the material did not distill. This residue was found to be soluble in ether and ligroin but was not investigated further.

The fraction boiling at 133–145° under 18 mm. pressure distilled at 233–246° under atmospheric pressure showing that it was beta-decahydronaphthol.

The second fraction (b.p., 230–245°) was heated with a 20% solution of sodium hydroxide. Addition of sulphuric acid to this reaction mixture caused the formation of about 1 g. of needle-shaped crystals which after recrystallization, first from ligroin and then from hot water, melted at 104–105°.

Anal. Calcd. for $C_{13}H_{19}O$: C, 83.7; H, 11.4. Found: C, 83.5; H, 11.8.

Heating these crystals with phenylisocyanate produced a crystalline substance melting at 187°. According to this data the substance was the phenylurethane of *beta-methylnaphthol.*

The third fraction (b.p., 255–270°) was a thick, viscous oil, honey-like in consistency and darkening rapidly on exposure to the air. By slow evaporation in air of its alcohol-ether solution, about 2 g. of crystals were obtained in the form of thin needles which after recrystallization from alcohol melted at 177–180°. These crystals dissolved in sulphuric acid and on slight heating formed a pink solution with a beautiful green fluorescence. A phenylurethane was not formed. Therefore, it must be concluded that a hydroxyl oxygen was not present in this product, although the data on its analysis indicated the presence of an atom of oxygen.

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[1] Leroux, Compt. rend., *140*, 590 (1905).

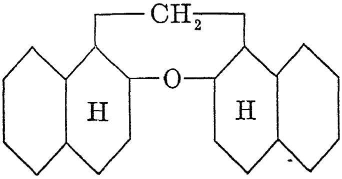
[2] Ipatieff, Ber., *40*, 181 (1907).

Anal. Calcd. for $C_{21}H_{22}O$: C, 86.9; H, 7.6. Found: C, 87.0; H, 7.7.

The crystalline substance was destroyed completely by oxidation with potassium permanganate, but we succeeded in detecting the formation of benzoic acid. The crystals were acted upon very energetically by nitrating mixture, but it was impossible to isolate a nitro compound. An attempt to determine the degree of hydrogenation by means of dehydrogenation, according to the method of Ruzicka gave the following results:

Anal. Calcd. for $C_{21}H_{22}O$: H, 0.065 g. Found: H, 0.072 g.

These analytical results correspond to ditetrahydronaphthylxanthene.



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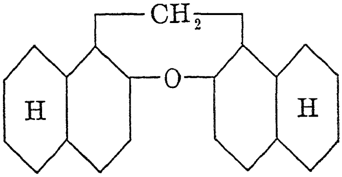

The remaining oil, as well as the rubber-like substance, contained an atom of oxygen, but these substances were not studied further.

Beta-beta-dihydroxydinaphthylphenylmethane.—This substance was synthesized according to the method of Hewitt and Turner [1] by condensation of beta-naphthol with triphenyl carbinol in a solution of acetic and hydrochloric (*d*, 1.19) acids. The writers recommended purification of the product from residual beta-naphthol and triphenyl carbinol by recrystallization from glacial acetic acid. This operation presented difficulties in large scale preparations because of the slight solubility of beta-beta-dihydroxydinaphthylphenylmethane. In boiling acetic acid a partial formation of xanthene was observed. Because of this behavior, an improvement was made in the preparation. The crystals were filtered off, placed in a flask containing water, the water was made alkaline with ammonia, and the mixture was heated on a water bath. After filtering, the crystals were washed three or four times with dilute alcohol and dried at 100–110°. The substance thus obtained melted at 197°.

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[1] Hewitt and Turner, Ber., *34*, 203 (1901).

Hydrogenation of the beta-beta-dihydroxydinaphthylphenylmethane was carried out at 250–280° according to the method previously described. In spite of the difference in temperature (as much as 30°) the same products were obtained, and about 1–3% of the gas present after hydrogenation consisted of paraffinic hydrocarbons. A clear, yellow oil with a slight greenish fluorescence was obtained at the end of the reaction. After the solvent (cyclohexane) was removed by distillation, an oil with a dark color and the odor of a mixture of tetralin and turpentine remained in the flask. This product could be treated in one of two ways, (1) by adding ligroin or petroleum ether in small portions to the oil, a layer of crystals could be separated, which increased in amount with time. These crystals, which were very slightly soluble in cold alcohol, after recrystallization from warm alcohol, melted at 167–168°. Steam distillation of the filtrate carried over a colorless oil, having an odor of hydrogenated naphthalene, which rapidly became yellow on standing. An additional quantity of crystals could be obtained from the viscous, rubber-like mass remaining in the flask by extraction in the cold with a mixture of alcohol and ether. (2) The second method was to steam distill the product of hydrogenation, but this treatment was not as satisfactory, since the crystals separated from the rubber-like mass with difficulty and their purification required many recrystallizations and led to large losses. The following results were obtained:

TABLE 67

	Weight, G.
Oil (Distilled with Steam)	70
Crystals	40
Distillate from Rubber-Like Substance in Vacuum	20
Solid Resin-Like Substance	75

The oil was divided into two fractions: (1) 185–215° (36 g.); (2) 220–250° (31 g.); the first fraction, 185–215°, was separated further into the following fractions:

TABLE 68

Fraction	B.P., °C.	n_D^{18}	d_{15}^{15}	Weight, G.
1	190–195	1.4843	0.9062	18
2	196–198	1.4890	0.9337	
3	200–204	1.5176	0.9542	5
4	204–213	1.5631	0.9852	10

Fractions 1 and 2 were subjected to hydrogenation at 270°. The product obtained had the same boiling point and properties as decalin: b.p., 189–190°; n_D^{18}, 1.4377; d_{15}^{15}, 0.8769.

Anal. Calcd. for $C_{10}H_{18}$: C, 87.0; H, 13.0. Found: C, 87.1; H, 13.3.

The 10 g. of fraction 4, boiling at 204–213°, was dehydrogenated by means of flowers of sulphur, producing naphthalene, from which the picrate melting at 149° was obtained.

The fraction boiling at 220–250° reacted vigorously when heated with sodium. With some of this fraction phenylisocyanate formed a phenylurethane melting at 163–164°. The fraction boiling at 230–240°, which was separated from the fraction boiling at 220–250°, solidified completely to a crystalline mass shown by analysis to be *beta-decahydronaphthol.*

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.9; H, 11.7. Found: C, 77.7; H, 11.7.

The oil remaining after separating the crystals was treated with sodium bisulphite for several days. The resultant white crystalline product, on decomposition by soda, yielded an oil of undetermined structure with the odor of mint.

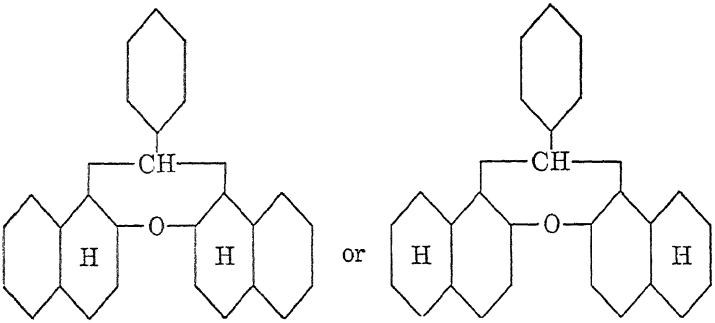
A total of 40 g. of crystalline beta-decahydronaphthol was obtained which after recrystallization from alcohol melted at 168°. It was insoluble in water and alkali; slightly soluble in alcohol, glacial acetic acid, and ligroin; readily soluble in ether, benzene, and cyclohexane. On heating slightly with sulphuric acid, the crystalline substance gave a pink coloration with a green fluorescence. Nitrating mixture converted it into a rubber-like substance. The reaction with sodium and the analytical data indicated the presence of oxygen, but a phenylurethane was not formed. It was inferred that this crystalline substance was a derivative of xanthene.

Anal. Calcd. for tetrahydronaphthylphenylxanthene:
C, 87.8; H, 7.3. Found: C, 88.3; H, 6.7.

In order to determine the degree of hydrogenation, a dehydrogenation was made by means of sulphur:

Anal. Calcd. for $C_{26}H_{26}O$: H, 0.0167 g. Found: H, 0.0168 g.

According to these data, probably ditetrahydrodinaphthylphenylxanthene was obtained.



The rubber-like substance remaining in the flask after distillation with steam gave the following fractions when distilled under 18 mm. pressure: (1) 145–190°; (2) 198–199°; (3) 208–210°. Beta-decahydronaphthol was isolated from the fraction boiling at 145–190° (18 mm.).

The fraction boiling at 198–199° (180 mm.) with d_{15}^{15}, 0.9738 was an oil of the consistency of glycerol which rapidly became colored.

Anal. Found: C, 85.5; H, 11.6; mol. wt., 362.

This fraction which was acted upon only slightly by nitrating mixture formed no phenylurethane. There is a possibility that this fraction was a mixture of xanthenes resulting from extensive hydrogenation.

From the fraction boiling at 145–190° (18 mm.) 8 g. of material was isolated having the following constants: b.p., 185–186° (18 mm.); d_{15}^{15}, 0.9806; n_D^{20}, 1.5249.

Anal. Found: C, 88.5; H, 11.5; mol. wt., 198.

No doubt this fraction was the *product of the hydrogenation of alpha-benzylnaphthalene* inasmuch as the above constants are very close to those of hydrogenated alpha-benzylnaphthalene.

The fraction boiling at 208–210° was a liquid of honey-like consistency which darkened on exposure to air. During the slow crystallization of this substance from a mixture of alcohol and ether, crystals of xanthene separated which melted at 167°. The oil remaining after separation of the crystals was analyzed for carbon and hydrogen.

Anal. Found: C, 88.4; H, 6.6.

These data closely approach the values for the composition of xanthene. As the oil did not form a phenylurethane, but did contain oxygen, it is necessary to assume that it was a mixture of products of various degrees of hydrogenation.

Diphenyl-alpha-naphthyl carbinol was obtained according to the method described by Acree,[1] starting with benzophenone and alpha-naphthylbromide (method of Grignard). The product after recrystallization melted at 133°.

During hydrogenation in the high pressure apparatus water separated and alpha-naphthyldiphenylmethane, a thick yellow mass, was formed. After recrystallization from a mixture of alcohol and ether, a pure hydrocarbon was obtained which melted at 149.5°. Further hydrogenation of this product at 280–290° in cyclohexane solution formed a yellow liquid with a slight purple fluorescence. After distilling off the cyclohexane, the remaining oil was separated by distillation into two fractions: (1) 182–210°; (2) 237–258°; residue, 260°.

The fraction boiling at 182–210°, after heating with concentrated sulphuric acid, followed by distillation over sodium, gave a clear oil with constants corresponding to those of decalin: b.p., 185–190°; d_{15}^{25}, 0.8796; n_D^{20}, 1.4720.

Anal. Calcd. for $C_{10}H_{18}$: C, 87.0; H, 13.0; mol. wt., 138. Found: C, 87.5; H, 13.2; mol. wt., 142.

The fraction boiling at 237–258° was a clear oil which, after washing with concentrated sulphuric acid, gave a fraction distilling at 246–252°; d_{15}^{15}, 0.8820; n_D^{20}, 1.4822. These analytical results indicate that the substance was *dicyclohexylmethane.*

Anal. Calcd. for $C_{13}H_{24}$: C, 86.7; H, 13.3; mol. wt., 180. Found: C, 86.6; H, 13.3; mol. wt., 182.

The residue boiling above 260° was distilled under 20 mm. pressure, giving the following fractions: (1) 144–147° (the remainder, dicyclohexylmethane); (2) 240–280° (a colorless, ice-like mass); (3) the residue, a rubber-like, black colored, mass.

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[1] Acree, Ber., *37*, 627 (1904).

CONCLUSIONS

(1) During the hydrogenation of dihydroxynaphthylmethane and dihydroxydinaphthylphenylmethane, water was eliminated with the formation of the corresponding xanthenes. These latter products on further hydrogenation added hydrogen and decomposed.

(2) Among the products formed, in addition to decalin, beta-decahydronaphthol, and derivatives, there were always present certain amounts of thick oils and rubber-like substances containing a non-hydroxylic oxygen atom.

(3) The rupture in the xanthene molecule took place in two directions.

(4) The bond of the naphthalene nucleus with the central carbon atom is much weaker than that between the central carbon atom and the benzene nucleus.

(5) Hydrogenation of diphenyl-alpha-naphthyl carbinol under pressure produced diphenyl-alpha-naphthylmethane which, on further hydrogenation, decomposed into naphthalene and dicyclohexylmethane.

HYDROGENATION OF ALDEHYDES AND KETONES

Hydrogenation of various classes of aldehydes and ketones was studied principally in the presence of nickel oxide, copper oxide, and mixed catalysts. The details of this work are described in the following pages.

Hydrogenation of Ketones of the Terpene Series

In order to clarify the question as to the course of hydrogenation of terpenic ketones possessing a double bond, hydrogenation experiments were made on *carvone, pulegone,* and *menthone* in the presence of nickel oxide.

Hydrogenation of Carvone.—The carvone was obtained from Kahlbaum and after distillation it had the following properties: b.p., 228–230°; d_{20}, 0.9596; n_D, 1.4922; $(\alpha)_D$, 35.05°.

Ketone (35–40 g.) and nickel oxide (3.5 g.) were introduced into the high pressure apparatus, hydrogen was pumped in, and the apparatus was heated in an electric oven. The results obtained in these experiments are listed in Table 69.

TABLE 69

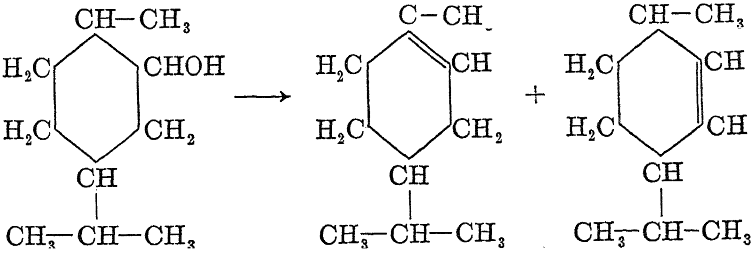
Expt. No.	Carvone Charged, G.	Press., Atms.		T., °C.	Time, Hrs.
		Initial	Final		
1	40	120		280	20
2	35	130	62	240	17
3	35	130	50	280	21
4	35	130	70	220	25
5	35	120	47	220	47
6	35	120	85	280	43

The product of Expts. 1 and 3 distilled almost completely at 218–222°. It was a thick, colorless oil with a menthol odor which did not decolorize potassium permanganate solution nor give crystalline compounds with sodium bisulphite, but it did, however, react with metallic sodium, liberating hydrogen. It had the following constants: d_{20}, 0.9002; $(\alpha)_D$, 0.50°; n_D, 1.45739; M.R., 47.24. According to its properties and analysis, the product was *carvomenthol.*

Anal. Calcd. for $C_{10}H_{20}O$: C, 76.8; H, 12.8. Found: C, 76.6; H, 12.7.

For the characterization of carvomenthol, it was converted into an unsaturated hydrocarbon according to the method of Ipatieff [1] which consists in splitting off water by means of alumina in the high pressure apparatus. The temperature of this dehydration was very high, namely, 360°; and the duration of the reaction was 4½ hours. The resulting hydrocarbon had the following properties: b.p., 160–165°; d_{20}, 0.8190; n_D, 1.45229; M.R., 45.48.

Excluding the possibility of displacement of the double bond as a result of the splitting out of water, the formation of two isomeric menthenes was possible:



The product of the second experiment (Table 69) had the following physical constants: b.p., 218–222°; d_{20}, 0.9068; $(\alpha)_D$, +16.93°; n_D, 1.45489; M.R., 46.04.

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[1] Ipatieff and Balatschinsky, Ber., *44*, 3461 (1911).

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.9; H, 11.7. Found: C, 77.5; H, 12.0.

It did not decolorize potassium permanganate solution but solidified into a compact crystalline mass when shaken with sodium bisulphite. According to its properties and analysis it might be concluded that at 240° the double bond alone is hydrogenated and that the ketone group remains intact, with the result that carvomenthone is formed.

The product obtained at 220° in the fourth experiment was not hydrogenated completely during the 20-hour experiment as shown by the fact that it decolorized potassium permanganate solution. But when the hydrogenation was continued for 40 hours at 220° in the fifth experiment, the double bond was hydrogenated completely and pure carvomenthone was obtained. The properties of this substance were almost identical with those of the ketone obtained in the second experiment: d_{20}, 0.9070; $(\alpha)_D$, +24.42°; n_D, 1.45429; M.R., 46.02.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.9; H, 11.7. Found: C, 77.7; H, 12.0.

However, attention is called to the fact that the specific rotatory power of the carvomenthone obtained at 220° is much greater than of that formed at 240°.

When the carvomenthone obtained in Experiments 2 and 5 was subjected to a further hydrogenation at 280° (Expt. 6), carvomenthol was the only product and it had the same properties as the substance resulting from the direct hydrogenation of carvone at 280°.

Hydrogenation of Pulegone.—Pulegone obtained from Kahlbaum showed the following constants when freshly distilled: b.p., 222–226°; d_{25}, 0.9328; $(\alpha)_D$, +29.81°; n_D, 1.47703; M.R., 46.04. Experiments made with pulegone gave the data tabulated in Table 70.

TABLE 70

Expt. No.	Pulegone Charged, G.	Press., Atms.		T., ° C.	Time, Hrs.
		Initial	Final		
1	35	120	62	280	20
2	30	110	74	220	31
3	30	100	70	220	33
4	35	100	66	240	24

The product of the first experiment was composed of two layers, the lower being water. The upper layer was extracted with ether and the extract was dried. After the ether was evaporated, the oily material was separated into two fractions by distillation: (1) 167–171° and (2) 200–212°. The first fraction, which did not decolorize potassium permanganate solution, had the composition corresponding to that of *menthane.*

Anal. Calcd. for $C_{10}H_{20}$: C, 85.7; H, 14.3. Found: C, 85.3; H, 14.2.

Since menthane was obtained in such large amounts under these conditions, it was clear that the temperature was too high for the formation of menthol, and therefore, further experiments were carried out at temperatures between 220° and 240°.

The product of Experiments 2 and 3 distilled almost completely at 205–210°; it was a colorless, mobile liquid with a pleasant peppermint odor which did not decolorize potassium permanganate solution and which gave no crystalline compound with sodium bisulphide. It had the following properties: d_{20}, 0.8972; $(\alpha)_D$, +21.39°; n_D, 1.44607; M.R., 45.78.

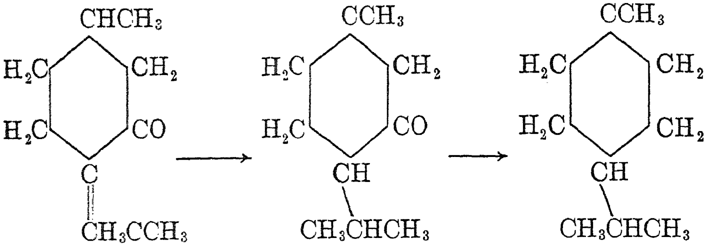
Anal. Calcd. for $C_{10}H_{18}O$: C, 77.9; H, 11.7. Found: C, 77.6; H, 11.8.

Upon the basis of these results, it follows that menthone is obtained in large yield by the hydrogenation of pulegone under these conditions. The hydrogenation proceeded much faster at 240° than at 220° producing menthone with the following properties: d_{20}, 0.8969; $(\alpha)_D$, +13.88°; n_D, 1.44587; M.R., 45.78. This menthone is distinguished from the menthone obtained at 220° only by its smaller specific rotatory power. The properties otherwise are identical.

These hydrogenation experiments show that at 220–240° pulegone adds hydrogen at the double bond forming menthone. The hydrogenation of the double bond and the conversion of the carbonyl group into an alcoholic group are not effected simultaneously by an increase in temperature because a reduction of menthone occurs under these conditions to form the hydrocarbon menthane.

In order to convert pulegone into *menthol,* it was decided to apply a step-wise hydrogenation, first to obtain menthone and then to hydrogenate it to menthol. Experiments confirmed the correctness of this decision. For this hydrogenation either the menthone obtained from pulegone or that purchased from Kahl-

45.21.



This menthone, when hydrogenated at 250° for 45 hours, gave a product boiling at 209–214° which contained no appreciable amounts of water. In order to insure complete hydrogenation, the product was heated under pressure with hydrogen at 210°, but only insignificant amounts of hydrogen were absorbed. The resulting product contained no water. After drying with fused potassium hydroxide, the product boiled at 212–213.5°. It was a thick, colorless oil with a strong menthol odor and had the following properties: d_{20}, 0.8948; $(\alpha)_D$, $-9.35°$; n_D, 1.45509; M.R., 47.32.

Anal. Calcd. for $C_{10}H_{20}O$: C, 76.8; H, 12.8. Found: C, 77.8; H, 13.0.

The product doubtless was *menthol*, which had a specific rotatory power opposite in sign to that of the starting menthone. This menthol solidified completely at $-10°$ and melted at $-8°$. According to its properties, it is similar to the menthol of Kondakow and Bachiew which had the constants: m.p., $-10°$; b.p., 215°; d_{20}, 0.9052; $(\alpha)_D$, 0°; n_D, 1.46445; M.R., 49.59.

Hydrogenation of Thymol.—In order to compare menthol from pulegone and from menthone with menthol obtained by hydrogenation of thymol, the latter was subjected to the action of hydrogen under high pressure in the presence of nickel oxide at 260° for 16 to 18 hours. Almost 90% of the product distilled at 210–220°. That part of the product which was unsaturated as shown by its reaction with potassium permanganate solution, was subjected to a second hydrogenation at 250–260°. No condensation products were formed and the whole product boiled at 212–216°. The fraction boiling at 211.5–213° which did not decolorize potassium permanganate solution possessed the following properties: m.p., 9°; fr.p., −10°; d_{20}, 0.8970; $(\alpha)_D$, 0°; n_D, 1.45659; M.R., 47.38.

According to its properties, this menthol is similar to the one which we obtained from menthone and the i-menthol of Kondakow and Bachiew. It is distinguished from another known i-menthol, that of Beckman[1] with melting point of 49–51°, which was obtained by heating phenylmethylurethane with sodium methylate at 150°.

Experiments of Ipatieff[2] show that although menthol is similar in structure to carvomenthol, it is much easier to dehydrate catalytically in the presence of alumina. From our menthol, in the presence of alumina, menthene ($C_{10}H_{16}$) was obtained in theoretical yield.

Conclusions

These experiments on the hydrogenation of terpenes lead to the following conclusions:

(1) By hydrogenation of terpenes at 220–240° in the presence of nickel oxide, complete hydrogenation of the double bond is effected whether it is present in the side chain or in the nucleus.

(2) Reduction of the carbonyl group to the hydroxyl group proceeds at 260–280°, but for terpenes of the type of menthone the temperature should not exceed 260° else menthane is formed.

(3) The lower the hydrogenation temperature, the greater the specific rotatory power of the hydrogenated terpenic material.

Hydrogenation of Unsaturated Aldehydes, Ketones, Diketones, and Alcohols[3]

Because of the great interest in the application of catalytic reactions in organic chemistry, various methods of hydrogenation have been developed, using different types of catalysts, especially reduced platinum and palladium whose catalytic ability has long been known.

The interesting experiments of Paal suggested to us the possibility of using catalysts in colloidal suspension for the hydrogenation of unsaturated hydrocarbons. Investigations by Fokin, Willstaetter, Tschugaeff, Skita, Vavon, Zelinsky, and others, showed that platinum black and reduced palladium are mildlyacting catalysts which permit the hydrogenation of unsaturated organic compounds at ordinary temperature without producing isomerization and decomposition reactions.

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[1] Beckman, J. prakt. Chem., (2), *55*, 30 (1897).

[2] Ipatieff, J. Russ. Phys. Chem. Soc., *38*, 42 (1906).

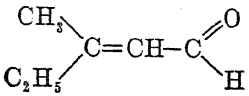
[3] Ipatieff, Ber., *45*, 3218 (1912).

At the request of Professor Chardin, who wanted to investigate the optical properties of α-methyl-α-ethyl-n-propyl alcohol (2, 2-dimethyl-1-butanol), I tried to prepare this alcohol according to the method proposed by Skita[1] in which β-methyl-β-ethyl-acrolein in aqueous alcoholic solution in the presence of palladium chloride and gum arabic is subjected to high pressure hydrogenation in the presence of excess hydrogen. The reaction did not take place at ordinary temperature or at 100° and at the end of the experiment we did not receive the alcohol but only the methylethyl acrolein and its condensation products.

From the results of these experiments, as well as those of the above-mentioned investigators, it is concluded that no universal method of hydrogenation has been devised due to the great difference between various classes of organic compounds. Thus, for example, the recent work of Willstaetter[2] shows that the hydrogenation of benzene in acetic acid solution in the presence of platinum black proceeds very slowly, although it ultimately quantitatively produces cyclohexane.

Hydrogenation with palladium reduced by formic acid under special conditions in the high pressure apparatus made possible the complete hydrogenation of certain very reactive compounds, usually at relatively low temperatures. The main difference between the present experimental procedure and that previously used was that mechanical stirring is now employed.[3] Stirring made possible a higher speed of hydrogenation and it also cut down the formation of condensation products. In the experiments previously mentioned, a great difference may be noticed between hydrogenation using the primitive method of shaking by hand and hydrogenation in which mechanical stirring was employed throughout the reaction.

Hydrogenation of β-Methyl-β-Ethyl Acrolein.—Methylethyl acrolein,



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[1] Skita, Ber., *42*, 1627 (1909).

[2] Willstaetter, Ber., *45*, 1471 (1912).

[3] Refer to Chapter I "Dehydrogenation," p. 32.

was obtained from propionic aldehyde by the action of sodium hydroxide according to Lieben's method. When hydrogenated at 130° in the presence of reduced nickel, many condensation products were formed and the yield of the alcohol was small, this being the reason for the use of palladium as catalyst.

One gram of palladium and 30 g. of freshly distilled propionaldehyde were placed in the bomb together with 110 atmospheres of hydrogen. The reaction was run at 110° for about two days, the apparatus being shaken from time to time. The reaction product contained a small amount of unchanged aldehyde and some condensation products. The distilled product (b.p., 142–155°) was subjected to a re-hydrogenation which resulted in the formation of pure 3-methyl-1-pentanol, $CH_3(C_2H_5)$-$CHCH_2CH_2OH$, which had the following properties: b.p., 145–146° (75 mm.); d_{18}, 0.8227.

Anal. Calcd. for $C_6H_{14}O$: C, 70.6; H, 13.7. Found: C, 70.8; H, 13.2.

The alcoholic product gave no reaction with bromine or with silver oxide and it did not decolorize a solution of potassium permanganate. The yield was good, but the reaction was very slow, and it was only when stirring was used (as may be seen from later experiments) that this reaction proceeded to completion in 2 to 3 hours.

Hydrogenation of Mesityloxide.—Mesityloxide, $(CH_3)_2C{=}CH$ $COCH_3$, could be hydrogenated in the presence of reduced palladium under high pressure but the reaction proceeded very slowly at 100° (1.5 to 2 days being required) and resulted in the formation of methylisobutyl ketone, boiling at 114–116°, with no tar. The hydrogenation of mesityl oxide at 145° proceeded very slowly also in the presence of reduced nickel under high pressure, equilibrium being established in about 4 days. The reaction product distilled at 114–134° and was a mixture of methylisobutyl ketone and methylisobutyl carbinol. In order to obtain the alcohol alone, it was necessary to raise the reaction temperature.

Hydrogenation of Citrals.—In spite of the fact that many methods have been proposed for the hydrogenation of the double bond in aliphatic compounds, there was only one previous experiment found on the hydrogenation of citral, that by Skita,[1] in which he was unsuccessful in obtaining the saturated alcohol *decanol,* though he did obtain a 33% yield of a mixture of *citronellal* and *citronellol:*

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[1] Skita, Ber., *42*, 1634 (1909).

$(CH_3)_2C{=}CH{-}CH_2{-}CH_2{-}C(CH_3){=}CH{-}CHO$, Citral (Geranial)

$(CH_3)_2C{=}CH{-}CH_2{-}CH_2{-}CH(CH_3){-}CH_2{-}CHO$, Citronellal

$(CH_3)_2C{=}CH{-}CH_2{-}CH_2{-}CH(CH_3){-}CH_2{-}CH_2{-}OH$, Citronellol

The remainder of the reaction products consisted of $C_{20}H_{34}O_2$, boiling at 139–140° (15 mm.), a condensation product of citral.

The hydrogenation of citral with reduced palladium at 110°, or with a mixture of reduced nickel and nickel oxide at 140° in the high pressure apparatus with continuous shaking proceeded very slowly (6–7 days). The following fractions were obtained at 15 mm. pressure: (1) 50–60° (25%); (2) 105–106° (50%); (3) 180–185° (25%).

The first fraction consisted of the saturated hydrocarbon *decane* ($C_{10}H_{22}$, 2, *6-dimethyl-octane*) which did not react with potassium permanganate solution. The second fraction, according to its analysis and properties, was not a single substance, but a mixture of decanol (2, 6-dimethyl-8-octanol) and certain unsaturated products which were not further studied.

Anal. Calcd. for $C_{10}H_{22}O$: C, 76.0; H, 13.9. Calcd. for $C_{10}H_{20}O$: C, 76.9; H, 12.8. Found: C, 77.1; H, 12.9.

In order to isolate decanol, the mixture was treated with phthalic anhydride according to the method of Stephans. The resulting alcohol distilled at 104–105° (12 mm.).

Anal. Calcd. for $C_{10}H_{22}O$: C, 76.0; H, 13.9. Found: C, 76.2; H, 13.3.

According to these data, the alcohol was decanol, but the yield was only about 10%.

The third fraction, boiling point 180–185°, was not studied.

The hydrogenation of citral proceeded in an altogether different manner when the high pressure apparatus was equipped with a mechanical stirrer. Thirty grams of citral was poured into a glass tube in which was 1 g. of reduced palladium; the glass tube was placed in the high pressure apparatus and 110 atmospheres of hydrogen was added. The apparatus was heated in a thermostat at 110°, the stirring arrangement being in operation during the entire time; the reaction was finished in 4 hours. The speed of the reaction can be realized from the fact that, in spite of heating, the pressure during the first 15 minutes increased only 6 atmospheres and that in the following minutes $(dp/dt)_{\max}$ was 2 k.m. The reaction product distilled almost completely at 107–108° (12 mm.), did not decolorize a solution of potassium permanganate, did not react with bromine, and according to its properties, was pure *decanol;* d_{18}, 0.8296.

Anal. Calcd. for $C_{10}H_{22}O$: C, 76.0; H, 13.9. Found: C, 76.5; 13.9.

Hydrogenation of Geraniol [$(CH_3)_2C{=}CHCH_2CH_2C(CH_3){=}CHCH_2OH$].—The hydrogenation of this alcohol was carried out by Willstaetter[1] according to Fokins' method by slowly passing the alcohol with hydrogen through a tube charged with platinum black. The above-mentioned decanol was obtained in 40% yield, the remaining 60% being decane. Enklaar[2] passed geraniol through a tube in the presence of reduced nickel at 103°, very slowly and with special care, obtaining decanol in small yield, and unsaturated products from which he isolated a cyclic alcohol to which he ascribed the structure of menthol.

I studied the action of reduced palladium at 110° and of a mixture of nickel oxide and reduced nickel at 135–140° in the high pressure apparatus which was shaken constantly, and found that both catalysts produced the same effect, though they acted rather slowly, about 5 days being required for the hydrogenation of 30 g. of material. Decanol was the chief product of the hydrogenation of geraniol, decane and condensation products being obtained in a small amount. The alcohol boiled at 105–106° (15 mm.); d_{18}, 0.8328.

Anal. Calcd. for $C_{10}H_{22}O$: C, 76.0; H, 13.9. Found: C, 76.6; H, 13.9.

After purifying this decanol according to the method of Stephans using phthalic anhydride, an alcohol was obtained which did not react with bromine, nor decolorize potassium permanganate solution. It boiled at 101–102° (10 mm.), and gave analytical figures corresponding to the formula $C_{10}H_{22}O$.

Anal. Calcd. for $C_{10}H_{22}O$: C, 76.0; H, 13.9. Found: C, 76.4; H, 13.9.

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[1] Willstaetter, Ber., *41*, 1478 (1908).

[2] Enklaar, Ber., *41*, 2084 (1908).

When stirring was employed, the reaction proceeded more rapidly and decanol [1] was the chief product, together with a small amount of decane. One gram of palladium was used for 40 g. of geraniol under 107 atmospheres of hydrogen; the reaction ran 6 hours at 110°. The first distillation (at 15 mm.) gave the following fractions: (1) 80–105° (4 g.); (2) 105–108° (24 g.).

According to its analysis and properties the second fraction was decanol: d_{18}, 0.8280.

Anal. Calcd. for $C_{10}H_{22}O$: C, 76.0; H, 13.9. Found: C, 76.6; H, 13.8.

Hydrogenation of Acetyl Acetone.—While using a stirring arrangement and reduced palladium as catalyst, it was also found possible to hydrogenate diketones, glycol appearing as the single reaction product. Thirty grams of acetyl acetone, boiling point 135–136°, and 1 g. of palladium were placed in a glass tube and subjected to hydrogenation under 116 atmospheres of hydrogen at 109° in the high pressure apparatus. After 6 hours the reaction was complete and the product, a thick pale yellow liquid, distilled almost without residue at 194–200°, the greater portion of it boiling at 197–198°. According to its properties and analysis, it was 2, 4-pentanediol: d_{18}, 0.9602.

$$CH_3{-}CO{-}CH_2{-}CO{-}CH_3 \rightarrow CH_3{-}CH(OH){-}CH_2{-}CH(OH){-}CH_3$$

Anal. Calcd. for $C_5H_{12}O_2$: C, 57.7; H, 11.5. Found: C, 58.1; H, 11.5.

Very different results were obtained when the hydrogenation of acetyl acetone was made at 135° in the presence of a reduced nickel catalyst in a high pressure apparatus which was merely shaken. The pressure decreased continuously for 40 hours, and the reaction product was a mixture consisting of unreacted acetyl acetone and methyl-n-propyl-ketone, the chief product of the reaction. It distilled at 102–104° and gave a crystalline compound with sodium bisulphite.

Anal. Calcd. for $C_5H_{10}O$: C, 69.8; H, 11.6. Found: C, 64.1; H, 11.4.

The formation of methyl-n-propyl ketone from acetyl acetone is difficult to explain, though perhaps it may be accounted for by the reduction of one of the carbonyl groups (of acetyl acetone). In all probability, it is to be assumed that the first hydrogenation product is a glycol from which at this temperature water may separate to form the oxide of dimethyltrimethylene glycol, the latter isomerizing with ease to methylpropyl ketone:

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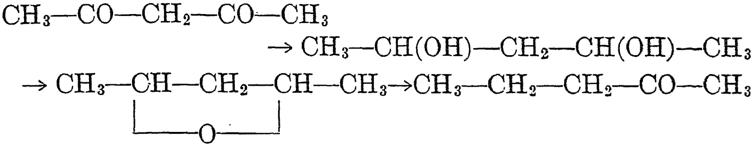
[1] The slightly higher content of carbon in the decanol obtained may be explained perhaps by the presence of *linalool*, $(CH_3)_2C{=}CH{-}CH_2{-}CH_2{-}C(OH)CH_3{-}CH{=}CH_2$, which might be obtained by the reversibility of the process; on repeated hydrogenation, it is converted into decanol.



$$CH_3{-}CO{-}CH_2{-}CO{-}CH_3 \rightarrow CH_3{-}CH(OH){-}CH_2{-}CH(OH){-}CH_3$$
$$\rightarrow CH_3{-}\underbrace{CH{-}CH_2{-}CH}_{O}{-}CH_3 \rightarrow CH_3{-}CH_2{-}CH_2{-}CO{-}CH_3$$

This assumption finds substantiation in the hydrogenation of the diketone, acetonyl acetone, $CH_3COCH_2CH_2COCH_3$, which hydrogenates in the presence of nickel at 190° at ordinary pressure to give hexylene oxide. It also indicates that the glycol which Sabatier and Mailhe [1] did not succeed in obtaining is the first product of the reaction and that this loses water to give the oxide with a 5-membered ring which is more stable than the 4-membered ring.

Hydrogenation of Carbohydrates [2]

The application of stirring in the high pressure apparatus made possible the hydrogenation of certain carbohydrates, namely, saccharides, to produce polyhydric alcohols in quantitative yields.

The well-known experiment of Emil Fischer on the reduction of monoses to the corresponding alcohols by means of sodium amalgam showed that this reaction proceeds very slowly and that considerable work is required to set the alcohol free. Preliminary experiments on the hydrogenation of certain monoses and bioses showed that catalysis offers the possibility of a very convenient method of preparation of polyhydric alcohols from the corresponding carbohydrates. It was found that not only reduced palladium, but also reduced nickel mixed with nickel oxide, may serve as excellent catalysts for the hydrogenation of carbohydrates to alcohols at 130–135°. The hydrogenation was carried out in aqueous-alcoholic solution, the concentration of the carbohydrate varying from 20 to 30%. The glass tube containing the saccharide solution and the catalyst was placed in the high pressure apparatus, and hydrogen was added up to 100 atmospheres pressure. The apparatus was then placed in a thermostat and the mechanical stirrer was set in motion. A temperature of 110° was required for palladium, 130–135° for nickel. Experiments showed that the reaction proceeded only when the stirrer was in operation, and ceased as soon as the stirrer stopped.

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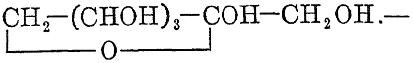
[1] Sabatier and Mailhe, Compt. rend., *144*, 1086 (1907).
[2] Ipatieff, Ber., *45*, 3224 (1912).



Hydrogenation of Fructose, $\underbrace{CH_2-(CHOH)_3-COH}_{O}-CH_2OH$.— A mixture of 10 g. of fructose (dissolved in 25 g. of water), 5 g. of alcohol, and 1 g. of palladium was heated for 3 hours at 108–109° under a hydrogen pressure of 84 atmospheres. A crystalline moss formed when the liquid product was evaporated on the water bath. The solid was dried on a porous plate and recrystallized. The substance thus obtained had the properties of d-mannite; m.p., 165–167°, and $(\alpha)_D$, 0.71°.

Anal. Calcd. for $C_6H_{14}O_6$: C, 39.6; H, 7.7. Found: C, 39.8; H, 7.7.

The reduction of fructose did not proceed to completion, the product still reacting slightly with Fehling's solution. Even when it was contacted with hydrogen 11 hours at 114°, it was not completely hydrogenated as evidenced by this test.

When reduced nickel was substituted for palladium in the aqueous-alcohol fructose solution, the hydrogenation proceeded just as well as in the case of palladium except that the temperature had to be raised to 130–135°. In this case also, the reaction was not complete since at the end of 24 hours of heating there were still traces of some substance which reduced Fehling's solution. An explanation of this phenomenon, as well as the evidence whether sorbite was also present in the reaction product in addition to mannite, will not be discussed at this time. However, it might be assumed that traces of some intermediate compound were formed which could be readily hydrogenated, giving monose which reacted with Fehling's solution. This assumption was partially confirmed by the experiments of Senderens [1] who repeated my experiments, employing a weak catalyst (a mixture of reduced nickel and nickel oxide ignited at 500°) and carried out the reaction in aqueous-alcohol solution at 120°. From lactose he obtained the intermediate product of the alcohol, "lactozitol."

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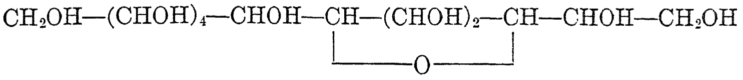
[1] Senderens, Compt. rend., *170*, 47 (1920).

$C_{11}H_{22}O_{11} + H_2 \rightarrow$



$$CH_2OH—(CHOH)_4—CHOH—\underbrace{CH—(CHOH)_2—CH}_{O}—CHOH—CH_2OH$$

Lactozitol was hydrolyzed by dilute acids into a mixture of sorbite and galactose. When a more active hydrogenation catalyst was taken, Senderens indicates that the intermediate product was not obtained; instead, a mixture of sorbite and dulcite was formed, as shown by my further experiments.

When, instead of a solution of fructose in aqueous-alcohol its solution in 95% alcohol was taken, the hydrogenation reaction proceeded very rapidly, and after cooling the apparatus, mannite separated in crystalline form.

The *hydrogenation of glucose* took place under the same conditions as in the case of fructose, but it went to completion as shown by the fact that the product did not reduce Fehling's solution. When reduced nickel was used, the reaction required 6–7 hours at 130–135°. After evaporation on a water bath to constant weight, a thick, colorless liquid was obtained which, on standing in a desiccator, solidified to a crystalline mass within 24 hours. According to its properties and analysis, the product was d-sorbite:

Anal. Calcd. for $C_6H_{14}O_6$: C, 39.6; H, 7.7. Found: C, 40.3; H, 8.1.

The sorbite obtained reacted in characteristic manner with benzaldehyde.[1] The yield of sorbite from glucose was excellent.

Reduction of Lactobiose.—Of the disaccharides, only lactobiose was investigated, the conditions for hydrogenation being the same as those for the monoses.

Ten grams of milk sugar and 1.5 g. of a catalyst mixture of nickel oxide and reduced nickel were heated under an initial hydrogen pressure of 74 atmospheres at 130–135° for 8 hours, the reaction being completed in this time. The liquid, on pouring from the glass tube of the apparatus, immediately deposited a large quantity of crystals which melted at 189–189.5°. According to their properties these crystals were *dulcite:* $(\alpha)_D$, 0°.

Anal. Calcd. for $C_6H_{14}O_6$: C, 39.6; H, 7.7. Found: C, 40.1; H, 7.9.

The liquid remaining after the separation of dulcite was evaporated on a water bath and converted into a thick syrup which did not crystallize even after a long standing.

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[1] Meunier, Compt. rend., *110*, 579 (1890).

HYDROGENATION OF DIBENZAL ACETONE AND DIBENZYL ACETONE[1]

Proceeding further on the foregoing basis, I[2] was able to show that hydrogenation under pressure with stirring offered the possibility of hydrogenating unstable organic compounds, such as unsaturated aldehydes, ketones, alcohols, etc., at low temperatures. This study concerned only aliphatic compounds. It now seemed interesting to study the hydrogenation of aromatic ketones under pressure by this method and dibenzal acetone was first chosen because it is easily obtainable and because it is a typical representative of ketones of this type.

Borsche,[3] Paal,[4] and Borsche and Wollemann[5] had studied the hydrogenation of dibenzal acetone in the presence of colloidal palladium at ordinary pressure, using benzene and alcohol as solvents. When complete saturation with hydrogen occurred, dibenzyl acetone was obtained in good yield; but when only partial hydrogenation took place the double bond was saturated and a small amount of crystallized product was also obtained.

Similar results would be anticipated with high pressure hydrogenation.

$$C_6H_5CH{=}CHCOCH{=}CHC_6H_5 \rightarrow C_6H_5CH_2CH_2COCH_2CH_2C_6H_5$$

It was interesting to ascertain the action of various catalysts. Copper oxide, which often is a very good catalyst for the hydrogenation of double bonds, could not be used in the present case. In spite of the use of a solvent, hydrogenation did not occur and all the ketone was converted into a thick, dark, tarry mass.

When nickel oxide was used as catalyst, an entirely different result was obtained, more than half of the ketone being converted into dibenzyl acetone, which was readily separated in pure state from the tarry products by vacuum distillation. It was noticed that the character of the solvent had a great influence upon the yield of the product. When using cyclohexane, in which dibenzyl acetone was only slightly soluble, this transformation did not take place. In spite of the absorption of hydrogen, the reaction product (after distilling off the solvent by means of steam) was a solid substance, fragile, transparent, amorphous, and readily decomposed by heat with the formation of unsaturated compounds which did not show a constant boiling point. This substance contained 84.9% of carbon and 10.4% of hydrogen. It differed from the tarry product which remained after the distillation of the product. The yield depended upon the concentration of the starting material.

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[1] Ipatieff and Orloff, Bull. soc. chim., *181*, 793 (1925).
[2] Ipatieff, Ber., *45*, 3218 (1912).
[3] Borsche, Ber., *45*, 46 (1912).
[4] Paal, Ber., *45*, 2221 (1912).
[5] Borsche and Wollemann, Ber., *45*, 713 (1912).

A benzene solution of 15% gave a 60% yield of product
" " " " 35% " " 25% " " "
" " " " 50% " " 10% " " "
" " " " 20% " " 20% " " "

The experiments were carried out in a high pressure apparatus equipped with a stirrer. The dibenzyl acetone was prepared by the condensation of benzaldehyde with acetone in an alkaline-alcoholic solution, according to the method of Strauss and Caspari.[1] The amount of nickel oxide catalyst was 15% by weight; the initial pressure was 70–100 atmospheres, the temperature 170–180°. The duration of the reaction was 24 hours, the reaction being considered complete when the pressure remained constant. After removal of the benzene, the product distilled at 209° under a pressure of 10 mm., and 335–340° at ordinary pressure. It crystallized on cooling. The recrystallized product melted at 13–14°; the observed molecular weight was 239, calculated 237.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.7; H, 7.6. Found: C, 85.6; H, 7.7.

The oxime was prepared by boiling the ketone with hydroxylamine hydrochloride for several hours, the latter being dissolved in 10 parts of alcohol containing several drops of hydrochloric acid. The melting point of the oxime was 91°.

In view of the contemplated study of some of the properties of dicyclohexyl paraffins, this ketone (dibenzyl acetone) was subjected to hydrogenation under pressure in cyclohexane solution in the presence of nickel oxide. The hydrogenation was run for 12 hours at 240°. After distilling off the solvent, an oil remained which was treated with fuming nitric acid in order to eliminate impurities. Pure *1, 5-dicyclohexyl pentane*, boiling at 315°, was obtained. This hydrocarbon did not decolorize potassium permanganate solution, nor did it react with nitrating mixture. It is evident, therefore, that the ketone was completely hydrogenated according to the equation:

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[1] Strauss and Caspari, Ber., *14*, 2460 (1881). This method is more convenient than that of Claisen because it gives a purer product in larger yield.

$C_6H_5CH_2CH_2COCH_2CH_2C_6H_5$

$+ H_2O$

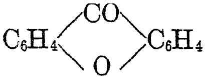
The substance possessed the following density and refractive constants: d_{20}, 0.8836; n_D^{20}, 1.478. It was identical with the hydrocarbon prepared by the hydrogenation of 1, 5-diphenyl pentane.

Anal. Calcd. for $C_{17}H_{32}$: C, 86.4; H, 13.6. Found: C, 87.1; H, 13.7.

HYDROGENATION OF XANTHONE AND XANTHENE [1]

My investigations [2] showed that aromatic ketones are easily reduced to the corresponding hydrocarbons by hydrogenation under pressure. Ipatieff, together with Philippoff,[3] showed that diphenyl ether ($C_6H_5OC_6H_5$), when hydrogenated under pressure in the presence of nickel oxide, gave chiefly cyclohexane and cyclohexanol accompanied by small amounts of a product resulting from a side reaction. In this hydrogenation the molecule ruptured at the oxygen-carbon linkage. This same point of rupture on hydrogenation was also observed with other hydrocarbons such as diphenyloxide.

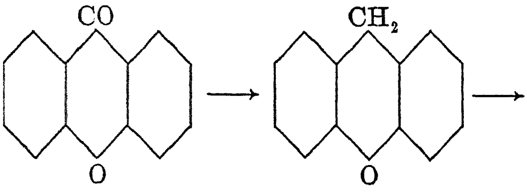
This observation induced us to study the hydrogenation of a substance having both ether oxygen and carbonyl group, attached to two benzene nuclei to form a heterogeneous ring. Such a compound, and one readily obtainable, is xanthone:



$$C_6H_4\left\langle\begin{matrix}CO\\O\end{matrix}\right\rangle C_6H_4$$

Hydrogenation experiments made under high pressure showed that hydrogenation took place in two phases, as follows:

(I)



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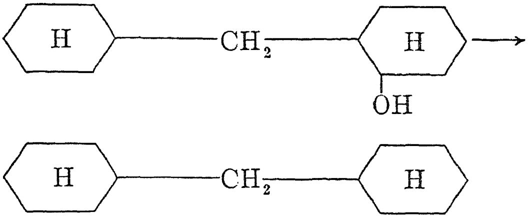
[1] Ipatieff and Orloff, Bull. soc. chim., *41*, 208 (1927).

[2] Ipatieff, J. Russ. Phys. Chem. Soc., *38*, 3875 (1906).

[3] Ipatieff and Philippoff, Ber., *40*, 996 (1908).

(II)



The carbonyl group was reduced to the methylene group with the formation of *xanthene*. Then hydrogenation of the benzene nuclei took place with rupture of the molecule at the oxygen linkage with the resultant formation of cyclohexylhydroxycyclohexylmethane. If high temperature was maintained during hydrogenation, or if the reaction was brought about in the presence of alumina and nickel oxide (joint action of catalysts), an unsaturated hydrocarbon [1] was obtained from this alcohol but it was not isolated. The hydrocarbon hydrogenated finally to dicyclohexylmethane.

Our first experiments [2] on the hydrogenation of xanthone were performed in the presence of a nickel oxide catalyst. The product was a mixture of xanthene, cyclohexylhydroxycyclohexylmethane, and dicyclohexylmethane. The yield of xanthene was greater at lower temperatures; at 212° xanthene was the chief product. In order to limit the reaction to the reduction of the carbonyl group and to prevent further transformations, the nickel oxide catalyst was replaced by copper oxide. Complete reduction of the carbonyl group took place with this catalyst, and xanthene was obtained in 92% yield. This method of preparing xanthene may successfully replace the method of Heller and Konstantsky which is inconvenient since it entails working with large amounts of material.

The xanthone used in the experiments was prepared in three different ways; from salol according to the method of Graebe,[3] by Perkin's reaction (action of acetic anhydride upon salicylic acid), and by the rapid heating of salol up to 440° in the high pressure apparatus. But, in spite of careful purification, the xanthone was always slightly yellow in color, although its melting point was 173.5°.

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[1] Ipatieff and Orloff, Compt. rend., *181*, 793 (1925).

[2] *Ibid.*

[3] Graebe, Ann., *254*, 281 (1889).

Hydrogenation of Xanthone with Copper Oxide

An intimate mixture of xanthone and 6 to 8% of its weight of copper oxide was prepared for the experiments and either benzene or cyclohexane was used as solvent. The initial hydrogen pressure was 100 atmospheres; the reaction temperature 250–260°; the time of heating 7–10 hours. After cooling, it was found that hydrogen had been consumed in theoretical amount and a crystalline substance, moistened by solvent, was present in the apparatus. With benzene as solvent, the solution was yellowish with a green fluorescence, but with cyclohexane the coloration was scarcely noticeable.

After removal of the solvent, the distilled xanthene was recrystallized from methyl alcohol from which pure, fragile, snow-white flakes (85–92% yield) were obtained. The product melted at 100.5° and boiled at 307–309° (749 mm.).

Anal. Calcd. for $C_{13}H_{10}O$: C, 93.7; H, 5.4. Found: C, 85.6; H, 5.5.

Hydrogenation of Xanthene with Nickel Oxide

Nickel oxide was added to xanthene, the former being 8% by weight of the latter and cyclohexane was used as solvent. The initial hydrogen pressure was 120 atmospheres, the duration of the experiment 8–20 hours, the temperature 270–290°. After the first hydrogenation, the product contained a small amount of unchanged xanthene, and it was therefore subjected to a second hydrogenation. After distilling off the solvent, the hydrogenation product was a thick liquid distilling at ordinary pressure at 260–280° with but little decomposition. Under reduced pressure (18–19 mm.), the product distilled at 157.5–158° as a thick liquid. After standing for several days, the liquid congealed to an oily mass melting at 40–43° and, once melted, it remained liquid for a long time; d_0^{40}, 0.9581.

Anal. Calcd. for $C_{13}H_{24}O$: C, 79.6; H, 12.2. Found: C, 79.9; 79.6; H, 12.2; 12.3.

Calcd. for $C_{13}H_{24}O$: mol. wt., 196; M.R., 58.3. Found: mol. wt. (fr.p., in benzene), 195; M.R., 58.7.

This substance had a strong odor similar to that of cyclohexylcyclohexanol, but more aromatic, especially when heated. It dissolved in sulphuric acid with a pinkish yellow coloration and was oxidized by an alkaline solution of permanganate on heating.

Sodium and potassium reacted energetically on heating to form alcoholates with liberation of hydrogen, and the alcohol was regenerated by the action of water. According to its analysis and properties, the product was a new alcohol, *hydroxydicyclohexylmethane.*

Hydrogenation of the Alcohol, Hydroxydicyclohexylmethane, in the Presence of the Mixed Catalyst, $Al_2O_3 \cdot NiO$

The alcohol obtained by the hydrogenation of xanthene in the presence of nickel oxide was subjected to further hydrogenation under pressure in the presence of a double catalyst, aluminum oxide—nickel oxide. The initial hydrogen pressure was 100 atmospheres, the temperature not above 300°, the time of reaction 5 hours.

The hydrogenation product yielded a fraction boiling at 248–254°. This fraction was heated on a water bath with sulphuric acid, washed with alkali, and redistilled over metallic sodium. The total product distilled at 250–252.5° (763 mm.); d_0^{20}, 0.8725.

Anal. Calcd. for $C_{10}H_{24}$: C, 86.6; H, 13.4. Found: C, 86.5; 86.3; H, 13.6; 13.4.

Cryoscopic determination of the molecular weight in benzene gave 179 as compared with the theoretical 180 calculated for dicyclohexylmethane; the yield, calculated on the xanthene, was 70%.

This hydrocarbon had practically no odor and did not react with nitrating mixture or with potassium permanganate solution. It was identical with the dicyclohexylmethane obtained by Eijkman [1] by the direct hydrogenation of diphenylmethane. This hydrocarbon was formed by the direct hydrogenation of *xanthene* with nickel oxide (without alumina) and the higher the temperature, the greater the conversion to the hydrocarbon. Thus, in one of the experiments at a temperature of 320–330°, up to about 60% of the xanthene was converted into dicyclohexylmethane within one or two hours.

Conclusions

The above experiments show that by proper choice of catalyst a selective hydrogenation of the heterocyclic ring can be effected.

[1] Eijkman, Chem. Weekblad, 1, 7 (1904).

(1) The copper oxide catalyst makes it possible to reduce the carbonyl group to the methylene group (CO to CH_2) and to pass from xanthone to xanthene, with excellent yield.

(2) By careful use of nickel oxide catalyst it is possible not only to hydrogenate, but simultaneously to isomerize the heterocyclic compound (xanthene) into a derivative (alcohol) of the diphenylmethane series. (See chapter on alkylation.)

(3) In the presence of a mixed catalyst containing alumina and nickel oxide, the heterocyclic compound is converted into a hydrogenated hydrocarbon, diphenylmethane.

HYDROGENATION OF ETHERS, ACIDS, AND ESTERS [1]

The preceding experiments showed that under hydrogen pressure, aromatic alcohols, aldehydes, and ketones are reduced to the corresponding hydrocarbons. Of course, if aromatic acids or their esters were hydrogenated under pressure, the formation of the corresponding hydrogenation products could not be obtained without rupture of the molecule at the oxygen bonds connecting the acid and alcohol radicals. But, in view of the interest in the study of the order of decomposition of these compounds under hydrogenation conditions, we were induced to carry out experiments on the hydrogenation of certain ethers and esters. Our assumptions (which were confirmed in part) were useful in leading to the discovery of a new method of hydrogenating aromatic acids.

Hydrogenation of Phenyl Ether

For this reaction, 20 g. of phenyl ether and 2 g. of nickel oxide under 100 atmospheres initial hydrogen pressure were heated at 230° for 10 to 12 hours until no further pressure decrease was observed. The quantity of hydrogen used was slightly greater than that required for complete hydrogenation of the two benzene nuclei; the gas remaining after the reaction was pure hydrogen. The reaction product consisted of a liquid which boiled between 80 and 270°. On distillation, two main fractions were separated: (1) 80–82° (cyclohexane); (2) 160–163°, which on standing solidified to a crystalline mass. The second fraction was pure cyclohexanol. Besides these two main fractions there was a third, small in amount, which boiled without decomposition at 275–277°

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[1] Ipatieff and Philippoff, Ber., *41*, 1001 (1908).

under ordinary pressure. This fraction was a thick liquid with a peculiar odor.

Anal. Calcd. for $C_{12}H_{22}O$: C, 79.1; H, 12.1. Found: C, 79.7; H, 12.5.

According to the analysis and properties, this fraction should be *cyclohexyl ether* which could be formed either by direct hydrogenation of phenyl ether, or from cyclohexanol by the splitting off of one molecule of water from two molecules of alcohol.

$$2C_6H_{11}OH \rightarrow C_6H_{11}OC_6H_{11} + H_2O$$

Cyclohexanol could be formed by hydrogenation of phenol, originating from the decomposition of phenyl ether into phenol and benzene, by the use of hydrogen and nickel oxide catalyst.

$$C_6H_5—O—C_6H_5 + H_2 \rightarrow C_6H_5OH + C_6H_6$$

Under these conditions benzene, as well as phenol, should hydrogenate to cyclohexane.

In order to determine whether cyclohexyl ether might be formed by the hydrogenation of phenol, a large quantity of the latter was subjected to the action of hydrogen under pressure in the presence of nickel oxide. After cyclohexanol was separated from the resulting product, a fraction was obtained boiling at 275–278°, which had the same odor and properties as the substance obtained by the hydrogenation of phenyl ether.

Anal. Calcd. for $C_{12}H_{22}O$: C, 79.1; H, 12.1. Found: C, 79.8; H, 11.3.

Thus, it may be assumed that phenyl ether first undergoes decomposition and that hydrogenation of the decomposition products continues, cyclohexyl ether being formed from cyclohexanol at a later stage.

Unfortunately, the conclusion regarding the structure of the product boiling at 275–278° was based on its analysis without giving proper attention to its high boiling point. Willstaetter and Hatt [1] and Schrauth and Wege [2] indicated that according to their investigations the product boiling at 275–278° was not cyclohexyl ether, but in all probability an isomerization product of it. Accordingly, Ipatieff and Orloff [3] undertook a detailed study of this fraction in order to definitely establish its structure.

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[1] Willstaetter and Hatt, Ber., *45*, 1464 (1912).

[2] Schrauth and Wege, Ber., *57*, 858 (1924).

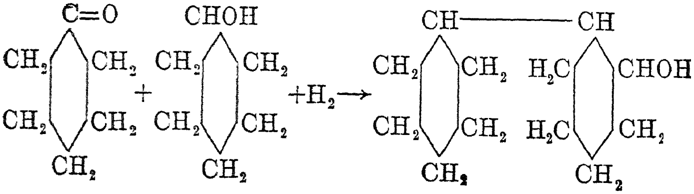
[3] Ipatieff and Orloff, Compt. rend., *180*, 793 (1925).

The product boiling at 275–278°, after being produced in sufficiently large quantity, was heated under hydrogen pressure in the presence of a mixed catalyst composed of aluminum hydrate and copper oxide. The reaction products consisted of a mixture of small amounts of *cyclohexylcyclohexene* and *dicyclohexyl.* Their separation was effected by heating the product with sulphuric acid and later treating with nitrating mixture. The dicyclohexyl thus obtained had the following properties: b.p., 237–238.5° (757 mm.); *d*, 0.8835. It was a slightly viscous, odorless, colorless liquid.

Anal. Calcd. for $C_{12}H_{22}$: C, 86.7; H, 13.2. Found: C, 86.4; H, 13.3.

The formation of these two products, especially the unsaturated hydrocarbon cyclohexylcyclohexene, showed that the substance boiling at 275° cannot be a cyclohexyl ether, but must be a cyclohexylcyclohexanol. This alcohol, under the influence of alumina, underwent dehydration to give an unsaturated hydrocarbon which, in the presence of the copper catalyst underwent further hydrogenation and was converted into dicyclohexyl.

The formation of cyclohexylcyclohexanol by hydrogenation of phenol and phenyl ether may be explained by a hypothesis which I proposed in 1905, namely, that involving the two tautomeric forms of phenol. This tautomerism furnishes the only possible explanation of the formation of cyclohexanone at a low temperature of hydrogenation.



As a means of testing the correctness of this assumption it was interesting to subject *diphenyleneoxide* to hydrogenation because in it, besides the usual linkage between the benzene nuclei, there is also an oxygen linkage.

The old method of Graebe [1] for the preparation of diphenyleneoxide was used because neither the method of Sabatier [2] nor that of Ferarior[1] gave satisfactory results. The diphenyleneoxide was thoroughly purified by passing its vapors over copper.

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[1] Graebe, Ann., *174*, 190 (1874).

[2] Sabatier, Compt. rend., *151*, 482 (1910).

The hydrogenation was made at 290° and 140 atmospheres of hydrogen in the presence of nickel oxide, using cyclohexane as solvent. The products of the reaction were the same as previously obtained. The dicyclohexyl had the following properties: b.p., 236–237.5°; d_{20}, 0.8919.

Anal. Calcd. for $C_{12}H_{22}$: C, 86.7; H, 13.2. Found: C, 86.8; H, 13.0.

Besides dicyclohexyl, a small amount of cyclohexylcyclohexanol was isolated. This is evidence that one of the bonds connecting the benzene nuclei and the oxygen atom was ruptured resulting in the formation of this alcohol through the action of hydrogen. A separation of water and the formation of an unsaturated hydrocarbon took place as well as further hydrogenation of the latter. The two samples of dicyclohexyl obtained in the two experiments described were not entirely identical; that is, they were slightly distinguishable from each other by their properties, such as odor, density, and boiling point which, in all probability, finds its explanation in the special stereochemical isomerism indicated by Schrauth and Göring,[2] as well as by Mohr.[3] After studying the alkylation of organic compounds it is now possible to offer a simpler explanation of the process and of the formation of cyclohexylcyclohexanol by the hydrogenation of phenol and phenyl ether. (Refer to chapter on alkylation.)

Hydrogenation of Complex Aromatic Esters

Twenty grams of the ethyl ester of phthalic acid together with 2 g. of nickel oxide were heated in the high pressure apparatus under an initial pressure of 100 atmospheres of hydrogen. The temperature varied from 250° to 300° and the experiments were continued until no further decrease in the hydrogen pressure was observed. At all these temperatures the hydrogen consumed was considerably less than that required for the transformation of the benzene nuclei into naphthenic nuclei. The gas remaining in the apparatus after completion of the reaction contained, in addition to hydrogen, carbon dioxide and methane. The proportion of the latter increased with rise in temperature.

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[1] Ferarior, Bull. soc. chim., *4* (9), 536 (1911).

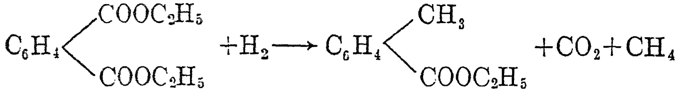
[2] Schrauth and Göring, Ber., *56*, 1900 (1923).

[3] Mohr, J. prakt. Chem., *97*, 315 (1918).

The liquid reaction product was extracted with ether; the extract was dried with calcium chloride and distilled. The following fractions were collected: (1) 220–250°; (2) 250–280°; (3) 280–290°. The first and third fractions were about the same in amount and considerably larger than the second fraction. Saponification of the first fraction yielded a solid acid which after recrystallization melted at 102–103°.

Anal. Calcd. for $C_8H_8O_2$: C, 70.6; H, 5.9. Found: C, 69.9; H, 6.1.

According to analysis, properties, and titration with $\frac{N}{20}$ potassium hydroxide solution, the acid was o-toluic acid formed in accordance with the following equation:



$$C_6H_4\left<\begin{matrix}COOC_2H_5\\ COOC_2H_5\end{matrix}\right. + H_2 \longrightarrow C_6H_4\left<\begin{matrix}CH_3\\ COOC_2H_5\end{matrix}\right. + CO_2 + CH_4$$

Saponification of the fraction boiling at 280–290° yielded a solid acid which, judged by its properties and melting point, consisted chiefly of phthalic acid. If there was any contamination by hexahydrophthalic acid, the amount of the latter must have been very small. When the ethyl ester of phthalic acid was hydrogenated at a higher temperature (325° to 350°) appreciable amounts of *benzoic acid* were obtained. By hydrogenation under the conditions indicated the esters of dibasic acids undergo reduction into the monobasic acids and, depending on the temperature, either benzoic or toluic acid is obtained.

Because the esters of aromatic acids could not be converted by hydrogenation into naphthenic acids, it was decided to make hydrogenation experiments directly on the salts of aromatic acids to see if naphthenic rings could be made this way. Our assumptions were found to be entirely justified and we were successful in discovering a new method for the hydrogenation of aromatic acids.

Hydrogenation of Potassium Phthalate

For the hydrogenation experiments, 20 g. of potassium phthalate which had been dried over sulphuric acid was triturated with 2–3 g. of nickel oxide. This solid mixture was heated for 9 hours at 300° under an initial hydrogen pressure of 100 atmospheres. At the end of the run and after the apparatus had cooled, the pressure had dropped to 23 atmospheres. This hydrogen consumption corresponded to an almost complete hydrogenation of the aromatic nucleus. The gas remaining in the cooled apparatus was hydrogen mixed with 2% of methane. The reaction product consisted exclusively of a solid salt which was dissolved in water, filtered from the nickel oxide, and decomposed with diluted sulphuric acid. The solid acid which separated was washed with water, dried, and then treated with chloroform to remove the small amount of benzoic acid present. However, the acid purified in this manner did not have a constant melting point. It melted between 196 and 215°, which is much higher than that corresponding to phthalic acid. To convince ourselves that the acid obtained contained trans-hexahydrophthalic acid, we prepared its calcium salt by saturation with lime water. There was an immediate precipitation of the insoluble calcium salt in large amount indicating that phthalic acid had been converted by hydrogenation into hexahydrophthalic acid. Analysis of the acids obtained in the various experiments gave confirmatory evidence.

Anal. Calcd. for $C_8H_{12}O_4$: C, 55.7; H, 7.0. Found: C, 56.1; 56.3; H, 6.7; 6.3.

The acid crystallized from water, in the form of plates; from acetone, in the form of needles. It did not decolorize a solution of potassium permanganate and eliminated water when heated above its melting point. In view of its indefinite melting point the acid was probably a mixture of the cis- and trans-isomers, perhaps contaminated with a slight amount of phthalic acid. The solid was dissolved in water, the solution was filtered, and the filtrate was evaporated to dryness on the water bath. The potassium salt was mixed with fresh nickel oxide and subjected to a second hydrogenation in order to remove the last traces of phthalic acid. After the second hydrogenation, the resulting acid was free from phthalic acid. At 300° only traces of benzoic acid were formed. The benzoic acid was readily extracted by chloroform in which hexahydrophthalic acid is insoluble. When phthalic acid was hydrogenated at a higher temperature, there was more methane in the residual gas and the reaction product contained more benzoic acid. At 350°, considerable benzoic acid was formed, the gases remaining after the experiment containing 32.2% methane and 66.8% hydrogen. The hydrogen consumed was about twice that required for complete hydrogenation of the aromatic nucleus.

Hydrogenation does not take place at ordinary pressure as shown by the following experiment. A mixture of potassium phthalate and nickel oxide was heated at ordinary pressure at 300–350° in a glass tube in a stream of hydrogen for 8 to 10 hours. At the end of the experiment, the acid separating from the salt was found to be unchanged phthalic acid.

Anal. Calcd. for $C_8H_6O_4$: C, 57.8; H, 3.6. Found: C, 58.1; H, 4.3.

Consequently, hydrogenation of phthalic acid in the presence of nickel oxide takes place only under pressure. As the reaction proceeds quite rapidly and gives a very good yield, it can be recommended as a satisfactory method for the preparation of hexahydrophthalic acid. Also, this method is much more convenient than others previously proposed for obtaining this acid.[1]

Hydrogen pressure alone was insufficient to effect the hydrogenation of phthalic acid as shown by experiments conducted in the absence of nickel oxide catalyst. Under such conditions, in spite of high temperature and pressure, no traces of hexahydrophthalic acid were obtained.

Hydrogenation of Potassium and Sodium Benzoates

Potassium benzoate dried in a desiccator over sulphuric acid was subjected to hydrogenation in the same manner as was potassium phthalate. The pressure decrease and the properties of the acid product showed, without doubt, that in this case also a hydrogenation of the aromatic nucleus had taken place with the formation of the salt of *hexahydrobenzoic acid.* Nevertheless, from a series of experiments conducted at various temperatures with a constant time factor it was ascertained that hydrogenation did not proceed to completion, but continued only to a certain limit, as evidenced by the fact that the hydrogenation product was always a mixture of hexahydrobenzoic acid and unchanged benzoic acid. About 40–50% of the benzoic acid underwent hydrogenation at 300–320°. On increasing the hydrogenation temperature to 400°, the gas remaining in the apparatus contained considerable methane and the yield of hexahydrobenzoic acid had diminished greatly. The yield of hexahydrobenzoic acid was increased but slightly by repeated hydrogenation.

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[1] A. von Baeyer, Ann., *259*, 214 (1890).

These experiments indicate that it is difficult to obtain large yields of the hydrogenated acid. For further experimentation, the sodium salt of benzoic acid was used. The first hydrogenation experiment on this salt showed a higher hydrogenation velocity of the aromatic nucleus than was observed with the potassium salt and as a result, even in the first hydrogenation, quite pure hexahydrobenzoic acid was obtained. The difference between the hydrogenation speeds of potassium and sodium benzoates may be seen from the following table:

TABLE 71

Potassium Benzoate			Sodium Benzoate		
Time, Min.	T., ° C.	Press., Atms.	Time, Min.	T., ° C.	Press., Atms.
	20	100		20	100
150	300	170	10	150	115
180	305	170	25	200	129
240	310	170	53	280	147
300	310	170	55	290	139
360	305	169	60	302	124
420	300	166	65	300	120
480	300	166	70	300	116
540	300	165	80	300	111
600	300	165	90	300	108
	20	90	120	300	107
			180	300	102
			240	300	100
			270	300	99
			300	300	99
			360	300	99
				20	58

From this table it is evident that hydrogenation of the potassium salt at 300° reaches its limit after 9 hours, while for the sodium salt this point is reached in 4 hours. The value of dp/dt reaches almost 5 kilo minutes for the sodium salt while it is insignificant for the potassium salt. Sodium benzoate hydrogenates almost as rapidly as does benzene in the presence of nickel oxide. Further experiments are necessary to explain this difference in the rates of hydrogenation of potassium and sodium benzoates.

The resulting sodium salt after hydrogenation was separated from the nickel oxide and decomposed with dilute sulphuric acid.

An oil separated which was extracted with ether; the extract was dried with calcium chloride and after removal of the ether, the material was distilled at ordinary pressure. The greater part of this substance boiled at 236–237° while only a relatively small fraction distilled at 240–248°. The first fraction consisted chiefly of hexahydrobenzoic acid, the second, mainly benzoic acid. Therefore, in order to prepare pure hexahydrobenzoic acid it is suggested that the sodium salt be subjected to two consecutive hydrogenations at 300°. The product obtained in such manner gave over 60% of *hexahydrobenzoic acid* distilling at 235–236° even on the first distillation. Analysis of this fraction gave the following results:

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.6; H, 9.4. Found: C, 65.8; 66.0; H, 8.9; 8.8.

The hexahydrobenzoic acid obtained was an oily liquid with an odor slightly reminiscent of valeric acid. On long standing, this oil crystallized in prisms melting at 30–31°. The crystals did not decolorize potassium permanganate solution. In general, it had all the properties of hexahydrobenzoic acid obtained by Aschan [1] and Markownikow.[2] Its characteristic *calcium salt* was obtained from the ammonium salt by precipitation with calcium chloride. This calcium salt is difficultly soluble in cold water, but readily crystallizes therefrom in needles with four and one-half molecules of water of crystallization. Analysis of the dried salt gave the following results:

Anal. Calcd. for $C_{14}H_{22}O_4Ca$: C, 57.1; H, 7.5; Ca, 13.6. Found: C, 56.9; H, 7.7; Ca, 13.5.

No hexahydrobenzoic acid is formed from sodium benzoate when hydrogenation is conducted at ordinary pressure at 300° in the presence of nickel oxide.

Because of its simplicity and good yields, the method of hydrogenating salts of mono- and dibasic aromatic acids in the presence of nickel oxide may successfully replace the old methods of hydrogenating acids by means of sodium in the presence of alcohol.

HYDROGENATION OF AROMATIC ACIDS IN THE PRESENCE OF NICKEL OXIDE AND COPPER OXIDE [3]

Work described in the preceding pages showed the possibility of hydrogenating salts of aromatic acids in the presence of nickel oxide to the corresponding naphthenic acids. Therefore, it was interesting to investigate other catalysts for this purpose. It had been demonstrated previously that olefin hydrocarbons could be hydrogenated under pressure in the presence of copper oxide or reduced copper. As the aromatic nucleus is not hydrogenated under these conditions it seemed desirable to investigate the possibility of hydrogenating double bonds present in the side chains of aromatic acids. Accordingly, the hydrogenation of cinnamic acid in the presence of copper oxide and reduced copper was studied, and also the action of hydrogen under pressure upon cinnamic acid in the presence of nickel oxide. Besides this, in order to show the possibility of hydrogenating aromatic acids containing condensed nuclei, the reaction with naphthoic acid was studied.

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[1] Aschan, Ber., *24*, 1865 (1891).

[2] Markownikow, Ber., *25*, 3357 (1892).

[3] Ipatieff, Ber., *42*, 2089 (1909).

Hydrogenation of Sodium Cinnamate

A mixture of 20 g. of sodium cinnamate and 3 g. of nickel oxide was placed in the high pressure apparatus into which hydrogen was pumped to a pressure of 106 atmospheres. The reaction was run at 300° for 12 hours. The cooled apparatus had a pressure of 55 atmospheres and the residual gas was pure hydrogen. The sodium salt was dissolved in water, decomposed with hydrochloric acid, and the separated acid was extracted with ether. After 24 hours, the ether was removed by distillation and the acid residue was distilled, practically all of it coming over at 275–278°. The acid from the first distillation was a colorless oil, solidifying in ice to a crystalline mass having the disagreeable odor of naphthenic acids. It did not decolorize potassium permanganate solution nor did it react with bromine. The acid obtained was the product of complete hydrogenation of cinnamic acid, namely, *β-cyclohexylpropionic acid.*

Anal. Calcd. for $C_9H_{16}O_2$: C, 69.2; H, 10.25. Found: C, 69.7; H, 10.1.

When the sodium salt of cinnamic acid was heated in the high pressure apparatus with hydrogen in the presence of 3 g. of reduced copper under the same conditions as above, in the course of the reaction only an insignificant decrease in the hydrogen pressure took place and, consequently, only a small amount of hydrogen added to the cinnamic acid. When the pressure within the apparatus had become constant the reaction product was extracted as described above. The combined acid from various experiments did not have a definite melting point. It decolorized a solution of potassium permanganate, and according to the analysis, it consisted of a mixture of *cinnamic acid* and *hydrocinnamic acid*, $C_6H_5CH_2CH_2COOH$.

Anal. Calcd. for $C_9H_{10}O_2$: C, 71.9; H, 6.7. Found: C, 73.2; H, 6.7.

For separation of the two acids, cold ligroin was used, a solvent in which the hydrocinnamic acid dissolved, leaving the cinnamic acid which was only slightly soluble, as residue. The hydrocinnamic acid, crystallized from ligroin in the cold, had an indefinite melting point (55–65°), decolorized the first few drops of potassium permanganate solution, and according to analysis, contained a certain amount of cinnamic acid. The acid difficultly soluble in ligroin was found to be cinnamic acid containing a small quantity of hydrocinnamic acid.

Anal. Calcd. for $C_9H_8O_2$: C, 73.0; H, 5.5. Found: C, 73.3; H, 5.8.

Thus, the hydrogenation of cinnamic acid in the presence of reduced copper as catalyst under a variety of conditions does not reach completion and the product always consists of a mixture of cinnamic acid and hydrocinnamic acid. In other words, it is a *reversible reaction:* $C_6H_5CH{=}CHCOOH + H_2 \rightleftarrows C_6H_5CH_2CH_2$-$COOH$. When commercial powdered copper oxide was used as catalyst for the hydrogenation of cinnamic acid, and the reaction was made under the above-mentioned conditions of high pressure, complete hydrogenation of cinnamic acid took place forming the salt of hydrocinnamic acid.

$$C_6H_5CH{=}CHCOOH + H_2 \rightarrow C_6H_5CH_2CH_2COOH$$

The acid melted at 48–49°, it did not decolorize potassium permanganate solution, and it was readily soluble in ligroin, from which it crystallized well.

Anal. Calcd. for $C_9H_{10}O_2$: C, 71.9; H, 6.7. Found: C, 72.1; H, 7.0.

These experiments on the hydrogenation of cinnamic acid in the presence of reduced copper and copper oxide showed that it makes no difference whether the catalyst is a finely dispersed reduced metal or its oxide. Because of the conditions under which the hydrogenation of cinnamic acid was carried out, that is, high pressure and high temperature, a part of the copper oxide was reduced to metallic copper and it is to be inferred that the reaction pursued the same course regardless of whether the initial catalyst was copper or copper oxide. Actually, an essential difference was observed in the hydrogenating action of those two catalysts, and this fact is sufficiently convincing that the hydrogenation and the dehydrogenation of organic compounds under the influence of various catalysts should be interpreted in many cases not by the formation of intermediate metallic hydrides, but by a participation of water in the catalytic process as stated in my first publication on the hydrogenation of alcohols.[1]

HYDROGENATION OF NAPHTHOIC ACIDS

Naphthalene was more difficult to hydrogenate under pressure in the presence of nickel oxide than was benzene. Likewise, from experiments on the hydrogenation of phenanthrene, anthracene, and other compounds, it may be concluded that polynuclear aromatic hydrocarbons are more difficult to hydrogenate than the mononuclear aromatic hydrocarbons, the former requiring higher temperature and repeated hydrogenations in order to obtain completely hydrogenated products. The same is true for acids containing several aromatic nuclei.

Hydrogenation of a naphthoic acid requires a higher temperature than does the hydrogenation of benzoic acid and the reaction must be repeated in order to obtain a completely hydrogenated acid. A difference is observed also in the end products of the hydrogenation of the two isomers (alpha and beta) of the naphthoic acids. While beta-naphthoic acid may be hydrogenated without decomposition, the alpha-naphthoic acid under similar conditions reduces to tetrahydronaphthalene (tetralin).

Hydrogenation of the Sodium Salt of Beta-Naphthoic Acid

The sodium salt of beta-naphthoic acid (β-$C_{10}H_7 \cdot COOH$) was hydrogenated in the high pressure apparatus in the presence of nickel oxide at 360° under an initial hydrogen pressure of 119 atmospheres. The duration of the experiment was approximately 50 hours. An acid separated at the end of the reaction which melted over a wide range. It was extracted in the cold with petroleum ether from which was obtained a small amount of a solid acid which melted from 70 to 90°. In all probability the product consisted of a mixture of naphthoic acids of different degrees of hydrogenation. The main part of the acid obtained by hydrogenation was insoluble in cold petroleum ether, melted at 143–144°, and did not react with bromine nor decolorize potassium permanganate solution. According to its analysis it was *tetrahydro-beta-naphthoic acid:*

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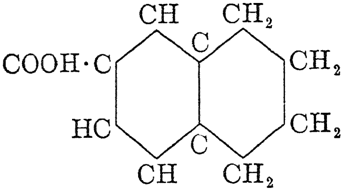
[1] Ipatieff, Ber., *34*, 3579 (1901).



Anal. Calcd. for $C_{11}H_{12}O_2$: C, 75.0; H, 6.8. Found: C, 75.4; H, 6.9.

The first hydrogenation of beta-naphthoic acid produced tetrahydro-beta-naphthoic acid. A second heating under hydrogen pressure at 340° caused further addition of hydrogen and formed the completely hydrogenated derivative of beta-naphthoic acid.

Hydrogenation of the sodium salt of *tetrahydro-beta-naphthoic acid* was carried out under the same conditions as the first hydrogenation of naphthoic acid. Two products were obtained, one a liquid and the other a salt. The liquid boiled at 200–202°. It did not react with potassium permanganate solution or with nitrating mixture. Its analysis corresponded to that of *decahydro-naphthalene* (decalin).

Anal. Calcd. for $C_{10}H_{18}$: C, 87.0; H, 13.0. Found: C, 86.9; H, 13.3.

From the salt the corresponding acid was obtained, which was an oily liquid. It solidified rapidly forming a crystalline mass which after separation in the usual manner and drying on clay plate melted at 79–81°.

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.5; H, 9.9. Found: C, 71.9; H, 10.1.

The acid did not decolorize potassium permanganate solution when dissolved in petroleum ether and it was considered to be *decahydro-beta-naphthoic acid,* originating as a reduction product of hydrogenated naphthoic acid. The hydrogen remaining in the apparatus after the hydrogenation contained about 6% of methane.

Hydrogenation of the Sodium Salt of Alpha-Naphthoic Acid

The sodium salt of alpha-naphthoic acid was subjected to hydrogenation at 350° in the presence of nickel oxide, but although the conditions were similar to these used with beta-naphthoic acid, quite different results were obtained. The reaction product consisted chiefly of a liquid hydrocarbon boiling at 215–220°, with the analysis and properties corresponding to *tetrahydronaphthalene.*

Anal. Calcd. for $C_{10}H_{12}$: C, 90.9; H, 9.1. Found: C, 91.5; H, 8.8.

A special experiment showed that naphthoic acids do not undergo hydrogenation at high temperatures and pressures in the presence of copper oxide.

HYDROGENATION OF AROMATIC ACIDS AND THEIR SALTS [1]

As stated above, the salts of aromatic acids can be hydrogenated under high pressure in the dry state in the presence of nickel oxide and converted into naphthenic acids. It has been observed that while potassium benzoate hydrogenates very slowly and incompletely, sodium benzoate hydrogenates readily, producing hexahydrobenzoic acid in 60% yield. Accordingly, it was interesting to investigate the behavior of other salts of benzoic acid, such as the lithium, calcium, barium, zinc, nickel, and ferrous salts in regard to their behavior with hydrogen under pressure. It was established that of the above benzoates only those of lithium, calcium, and barium could be hydrogenated. Zinc, nickel, and ferrous benzoates, when mixed with nickel oxide and subjected to hydrogenation in the high pressure apparatus underwent a far-reaching decomposition. The residual gas contained large amounts of methane and carbon dioxide. In the colder parts of the tube of the high pressure apparatus an intensely red sublimate formed which on exposure to air rapidly became brown. This substance plugged the tube leading to the pressure gage and thus interfered with the proper operation of the experiments. No detailed investigation of this substance was made.

The results of these hydrogenation experiments are summarized in the following table. The reaction velocities are shown by the curves in Figs. 25 and 26.

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[1] Ipatieff, Ber., *41*, 1001 (1908).

TABLE 72

HYDROGENATION OF METALLIC SALTS OF BENZOIC ACID

BENZOATE OF	T., ° C.	INITIAL HYDROGEN PRESS., ATMS.	PRODUCTS
Sodium	290	80	60% sodium hexahydrobenzoate, sodium carbonate, benzene, and cyclohexane; about 2% of methane in the gas
Potassium	300	80	Only an insignificant amount of the salt underwent hydrogenation with the formation of potassium hexahydrobenzoate
Lithium	275	80	60% lithium hexahydrobenzoate; lithium carbonate; benzene and cyclohexane; 1 to 2% methane in the residual gas
Calcium	270	80	60% calcium hexahydrobenzoate; about 1% carbon dioxide in the gas
Barium	275	80	60% barium hexahydrobenzoate
Zinc	350	80	Red sublimate in the colder parts of the apparatus; 15% methane in the gas
Nickel	300	80	Red sublimate in the colder parts of the apparatus; 6 to 7% methane and 2% carbon dioxide in the gas
Iron	300	80	Red sublimate in the colder parts of the apparatus

It is evident, therefore, that the course of the hydrogenation of the salts of benzoic acid depends upon the metal constituent of the salt.

HYDROGENATION OF HYDROXY ACIDS AND THEIR SALTS

A study was made of the hydrogenation of hydroxy acids containing an hydroxyl group in the aromatic nucleus, as well as in the side chain. The substances studied were: (1) *salicylic acid*, *para-hydroxybenzoic acid*, and (2) *mandelic acid.*

In the first case, the aromatic nucleus hydrogenated very rapidly and the carboxyl group split off simultaneously.

The hydrogenation of sodium salicylate was very rapid at 275–290° (Fig. 2). The residual gas contained 40% of methane and 1 to 2% of carbon dioxide. The COONa group was removed by the hydrogenation with the formation of sodium carbonate, water, and carbon dioxide, the latter being reduced to methane. The phenol formed by the elimination of the COONa group was hydrogenated immediately, giving chiefly *cyclohexanol* and also insignificant amounts of high boiling products, probably cyclohexylcyclohexanol. No cyclohexanone was formed.

Hydrogenation of free salicyclic acid, as well as of p-hydroxy benzoic acid proceeded much more slowly, requiring more than 48 hours for its completion. The reaction took place according to the following equation:

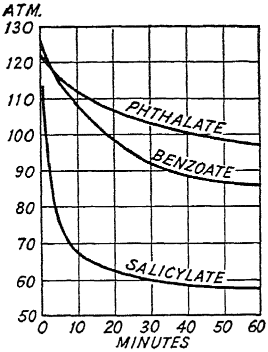


FIG. 25

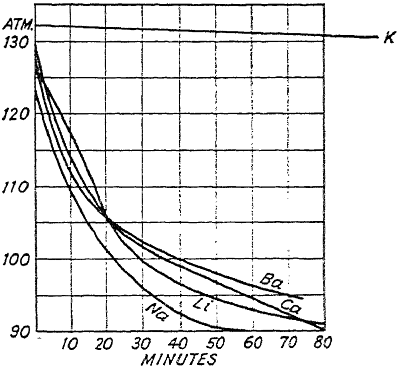


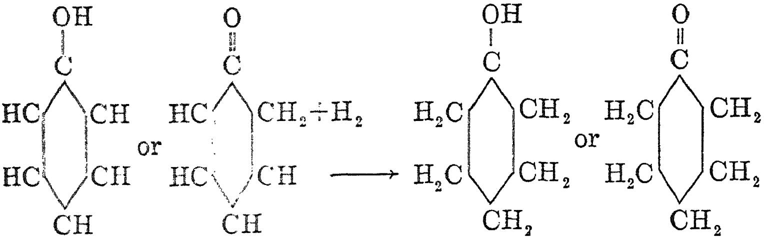
FIG. 26

$$C_6H_4(OH)COOH + 3H_2 \rightarrow C_6H_{11}OH + CO_2$$

The product obtained was pure cyclohexanol, free from cyclohexanone. Cyclohexanol was isolated from the hydrogenated product by distillation, and crystallized. According to Ipatieff, a considerable quantity of cyclohexanone in addition to cyclohexanol is always formed when phenol is hydrogenated under pressure. The lower the hydrogenation temperature, the greater the yield of cyclohexanol. As an explanation for the formation of this abnormal product, it is assumed[1] that hydrogenation acted upon the two tautomeric forms of phenol, enolic and ketonic, one of which hydrogenated to cyclohexanol, the other to cyclohexanone.

Hydroxybenzoic acids do not exist in the keto-form and, therefore, from these only one hydrogenation product, cyclohexanol, is obtained.

[1] Ipatieff, J. Russ. Phys. Chem. Soc., *38*, 89 (1906).



Free mandelic acid, $C_6H_5CH(OH)COOH$ cannot be hydrogenated since it decomposes to tarry products. Under hydrogenation conditions, sodium mandelate suffers reduction of the hydroxyl group and *phenylacetic acid* is formed. A further partial hydrogenation occurs with the formation of *cyclohexylacetic acid* melting at 26°.

A mixture of 20 g. of dry sodium mandelate and 3 g. of nickel oxide was placed in a high pressure apparatus of 280 cc. capacity, hydrogen being pumped in to about 80 atmospheres pressure. A double hydrogenation was made in order to obtain an homogeneous product. The aqueous solution of the product, after separation from the catalyst by filtration, was decomposed by hydrochloric acid and the precipitated acid was extracted with ether. After removal of the ether the acid distilled at 234–236°, solidified at room temperature to a crystalline mass, and had the characteristic odor of hexahydrobenzoic acid.

Hydrogenation of Sodium Salicylate.—This hydrogenation experiment was carried out at 280–290°, the other conditions being those indicated above. At the end of the reaction the tube contained a mixture consisting of nickel carbonate, cyclohexanol, and water. The most convenient method to separate cyclohexanol was by steam distillation. The distillate of oil and water was extracted with ether; the ether was distilled from the solution and, finally, the extract was distilled. Sixty-nine grams of this product yielded 61 g. boiling at 159–163° (cyclohexanol) and about 7 g. boiling at 260–280°.

Hydrogenation of Salicylic Acid.—This hydrogenation was carried out in a high pressure apparatus of one liter capacity. A mixture of 100 g. of salicylic acid and 10 g. of nickel oxide under 90 atmospheres initial hydrogen pressure was heated at 275–290° for 60 hours. After cooling, the pressure in the apparatus was 25 atmospheres. The residual gas contained about 15% of carbon dioxide and methane. The thick liquid was poured from the apparatus and dissolved in ether. The solution was filtered from the catalyst, and dried. After removing the ether by distillation, the entire substance with the exception of a small tarry residue distilled at 159–161°. The yield of cyclohexanol was 87.2% of the theoretical.

Anal. Calcd. for $C_8H_{12}O$: C, 72.0; H, 12.0. Found: C, 72.1; H, 12.1.

Hydrogenation of p-Hydroxybenzoic Acid.—This hydrogenation was identical in behavior with that of salicylic acid discussed above.

Hydrogenation of Sodium Mandelate.—In a high pressure apparatus of one liter capacity a mixture of 45 g. of the salt and 7 g. of nickel oxide under 84 atmospheres initial hydrogen pressure was heated at 280° for 14 hours. After cooling, the pressure in the apparatus was 20 atmospheres. The residual gas contained 86% of hydrogen and 13% of methane. The apparatus contained a thick mass consisting of salt, catalyst, and water. The salt was extracted with water and the resulting solution was treated with hydrochloric acid which resulted in the evolution of carbon dioxide and the separation of a visible layer of acid. The low boiling acid was distilled with steam from the phenylacetic acid which melted at 76° after numerous recrystallizations.

Anal. Calcd. for $C_8H_8O_2$: C, 70.6; H, 6.0. Found: C, 70.5; H, 6.2.

The yield of phenylacetic acid was about 40% of the theoretical amount. The acid was distilled with steam and was extracted from the distillate with ether. After the ether had been evaporated, this material solidified on standing to a crystalline mass possessing sharp odor and a melting point of 26°.

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.8; H, 9.8. Found: C, 67.6; H, 9.9.

According to the analysis and properties the acid should be considered *cyclohexylacetic acid.*

HYDROGENATION OF SALTS OF AROMATIC ACIDS[1]

In the preceding pages it was shown that very small amounts of benzene and cyclohexane are obtained in the hydrogenation of sodium benzoate, but in the hydrogenation of sodium mandelate under the same conditions, much larger amounts of hydrocarbons are formed and the yield of phenylacetic acid does not drop below 40%. The essential difference in the hydrogenation of the salts of these two acids is due to the fact that mandelic acid forms first phenylacetic acid which decomposes in the presence of water, after which hydrogenation continues. In order to understand the influence of water in the hydrogenation of salts, a series of parallel hydrogenation experiments was made with dry salts and with their solutions.

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[1] Ipatieff and Razuvaev, Ber., *59*, 2028 (1926).

The experimental results showed that hydrocarbons are formed in both cases, but that the yield of hydrocarbon is greater from the dissolved salt. Also, the acids obtained by the hydrogenation of the dissolved salts are completely hydrogenated.

The formation of hydrocarbons by hydrogenation might be expressed by the following equation:

$$2RCOONa + 4H_2 \rightarrow 2RH + CH_4 + Na_2CO_3 + H_2O$$

This reaction proceeds independently of the other hydrogenation reactions.

$$C_6H_5COONa + 3H_2 \rightarrow C_6H_{11}COONa$$

Water is a favorable medium for the first, as well as for the second reaction. Other solvents exert a similar influence in the process of hydrogenation. For example, in the case of methyl salicylate there is no hydrogenation in the absence of solvent, only small amounts of phenol and much tarry residue being formed. But when the hydrogenation of this ester is made in alcohol solution, the reaction proceeds smoothly and cyclohexanol is obtained in almost theoretical yield. During the hydrogenation of aliphatic acids, catalytic decomposition of the carboxyl group also takes place. Thus, when heated with nickel oxide up to 300° under hydrogen pressure, sodium acetate solution decomposes and forms methane and sodium carbonate equivalent to 40% of the theoretical.

$$2CH_3COONa + 4H_2 \rightarrow Na_2CO_3 + 3CH_4 + H_2O$$

Sodium Benzoate.—As previously indicated, dry sodium benzoate in a single hydrogenation yields about 60% of acids boiling from 233 to 250° which consist of a mixture of hexahydrobenzoic and benzoic acids. From 50 g. of salt, 2.5 g. of benzene was formed, and 2% of methane was found in the residual gas.

The results were entirely different when the salt was hydrogenated in aqueous solution. In this experiment 50 g. of sodium benzoate, 75 cc. of water, and 7 g. of nickel oxide were heated at 300° under an initial hydrogen pressure of 92 atmospheres. The residual gas contained 9.7% of methane and 90% of hydrogen. Nine grams of cyclohexane[1] boiling at 79–80° was obtained and pure *hexahydrobenzoic* acid boiling at 235–238° was isolated in 40% yield. Such a yield of acid can be obtained only by repeated hydrogenations in the dry state.

Sodium Mandelate.—As mentioned above, the hydrogenation of the dry salt gave a mixture of *phenylacetic acid* and *cyclohexylacetic acid.* On further hydrogenation, the mixture was converted completely into cyclohexylacetic acid, b.p., 243–248°, and m.p., 28°. Almost one-half of the dry salt decomposed with the formation of a hydrocarbon mixture boiling at 90–105° which was shown by analysis to consist of *toluene* and *hexahydrotoluene.*

Hydrogenation of sodium mandelate in aqueous solution (50 g. of salt in 75 cc. water) in the presence of nickel oxide (7 g.) at 275–286° under 80 atmospheres initial hydrogen pressure gave a mixture of hydrocarbons from which the following fractions were obtained on distillation: (1) 80–90° (2 g.); (2) 90–107° (14 g.); (3) 107–110° (3 g.). These fractions had the following properties and analyses:

TABLE 73

FRACTION	d_0^{18}	n_D^{18}	ANAL., C.	% FOUND, H
1	0.7994	1.4423	87.2	12.6
2	0.8198	1.4607	88.9	10.8
3	0.8572	1.4858	90.5	9.4

The main part of the mixture consisted of *hexahydrotoluene* mixed with small amounts of toluene and probably cyclohexane. Only 2 g. of acid separated from the solution. This acid boiled at 243°, melted at 30°, and possessed the properties of *cyclohexylacetic acid.*

Sodium Phenyl Acetate.—Hydrogenation of a mixture of 15 g. of the dry salt and 2 g. of nickel oxide at 270° under an initial pressure of 80 atmospheres gave an acid as the chief product of the reaction. The residual gas contained 1% of methane. Hydrocarbons were formed in very small amount (b.p., 105–109°) which resembled in properties the hydrocarbons obtained from sodium mandelate. The acid which was obtained (6.5 g.) distilled at 244–248°, and melted at 30°. On the basis of its properties and analysis it was identified as *cyclohexylacetic acid.*

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[1] The cyclohexane contained only traces of benzene.

Under similar conditions the hydrogenation of 15 g. of the salt dissolved in 50 cc. of water gave 7.2 g. of hydrocarbon boiling at 106–110° as the main product of the reaction. This hydrocarbon appeared to be similar to that obtained from the dry salt. Only 1 g. of *cyclohexylacetic acid* was obtained; m.p., 29°.

Sodium Cinnamate.—Hydrogenation of 50 g. of the dry salt yielded about 60% of an acid product boiling at 266–270°, evidently a mixture of *beta-cyclohexylpropionic acid* and *hydrocinnamic acid.*[1] Only 2 g. of hydrocarbon boiling at 125–130° was obtained. There was a very small amount of *methane* present in the gas.

Hydrogenation of 50 g. of sodium cinnamate dissolved in 100 cc. water in the presence of 5 g. nickel oxide under an initial hydrogen pressure of 95 atmospheres gave 15.5 grams of a hydrocarbon boiling at 130–135°, d_0^{20}, 0.8359, and n_D^{20}, 1.4703. Analysis showed: C, 87.9; H, 11.7. From the solution was isolated an acid boiling at 268–270° which consisted of *beta-cyclohexylpropionic acid* contaminated by a very small amount of hydrocinnamic acid. This product, after a second hydrogenation, gave pure cyclohexylpropionic acid melting sharply at 8°. The yield of acid was 45% of the theoretical amount.

Sodium Acetate.—After heating a solution of 50 g. of sodium acetate in 100 g. of water in the presence of 5 g. of nickel oxide under 80 atmospheres initial hydrogen pressure at 300°, the resulting gas contained 9.5% methane. Analysis of the remaining salt showed that 35 to 40% of the sodium acetate had decomposed.

Sodium Heptoate.—A solution of 25 g. of the salt in 70 cc. of water was heated at 315° in the presence of 3 g. of nickel oxide under less than 90 atmospheres initial hydrogen pressure. Approximately 25% of the salt decomposed; *methane* and *hexane* (b.p., 68–72°) were formed:

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[1] The conclusion drawn in 1909 from experiments on the hydrogenation of cinnamic acid in the presence of nickel oxide must be corrected slightly because the cyclohexylpropionic acid obtained at that time contained a small amount of hydrocinnamic acid. Repeated hydrogenation gave pure cyclohexylpropionic acid.

$$2CH_3—(CH_2)_5—COONa + 4H_2 \rightarrow 2C_6H_{14} + CH_4 + Na_2CO_3 + H_2O$$

Methyl Salicylate.—When 100 g. of this ester was hydrogenated for 3 days without solvent in the presence of nickel oxide at 280°, 38 g. of phenol and a resinous residue were obtained. When the hydrogenation was carried out under the same conditions, but in methanol solution (65 g. of ester in 65 g. of methanol), the reaction proceeded in a different manner, producing 40 g. of a thick, transparent liquid; b.p., 160–161.5°; d_0^{18}, 0.9542; n_D^{20}, 1.4688. This product was *cyclohexanol.* It was free from phenol as evidenced by the non-coloration with ferric chloride; on cooling it solidified to a crystalline mass.

Anal. Calcd. for $C_6H_{12}O$: C, 72.0; H, 12.0. Found: C, 71.8; H, 11.8.

CONCLUSIONS

The following conclusions may be drawn from the experiments made on the hydrogenation of acids and their salts.

(1) Hydrogenation is a convenient method for converting salts of the aromatic acids into naphthenic acids.

(2) With proper choice of catalyst the unsaturated side chain of an aromatic acid can be hydrogenated without affecting the aromatic nucleus.

(3) Hydrogenation of salts of aromatic acids having carboxyl and hydroxyl groups attached to the aromatic nucleus causes a splitting off the carboxyl group, but the hydroxyl remains unaltered.

(4) When both carboxyl and hydroxyl groups are present in the side chain, the carboxyl group is stable to hydrogenation, but the hydroxyl group is reduced.

(5) Hydrogenation of salts of the aromatic acids in aqueous solution is entirely different than the hydrogenation of the dry salts. In aqueous solution the hydrogenation of the acid is accompanied by a certain amount of decomposition and the resultant formation of hydrogenated hydrocarbons whereas in the dry state there is no formation of hydrocarbons.

HYDROGENATION OF FATS IN THE PRESENCE OF NICKEL OXIDE AND REDUCED NICKEL[1]

Through my study of the hydrogenation of various aromatic and unsaturated organic compounds under high pressure, I was the first[2] to show that it is preferable to use the oxides of nickel rather than the reduced metal to effect the catalytic addition of hydrogen. The speed of hydrogen addition is greater in the presence of the oxides than it is in the presence of previously reduced metal.

In searching for an explanation regarding the rôle of oxides in the phenomena of reduction and oxidation catalyses, a series of experiments[3] was undertaken which proved to me the correctness of my hypothesis concerning catalytic dehydrogenation and hydrogenation of organic compounds. In addition, these experiments indicated the very interesting fact that in spite of the high temperatures and high pressures of hydrogen, the reduction of the nickel oxides used as catalyst is not complete. The nickel content of used catalyst is not much higher than that of the original catalyst. In all cases, however, used catalyst contained metallic nickel as shown by the action of nitric acid (*d*, 1.4). However, my experiments did not entirely clarify the question as to the cause of the high speed of hydrogenation in the presence of nickel oxide and I offered only an assumption to the effect that possibly the reduction of nickel oxides is limited to the formation of lower oxides which may accomplish the same purpose as the reduced nickel. From the standpoint of my hypothesis these lower oxides may accelerate the speed of the reaction more than reduced nickel.

My experiments showed that a given sample of nickel oxide catalyst can serve many times in the hydrogenation of unsaturated compounds and is distinguished from nickel prepared according to Sabatier and Senderens for hydrogenation at ordinary pressure by its non-sensitiveness to various poisons. Moreover, it should be noted that in high pressure catalytic reduction by my method, the purity of the nickel oxide and its method of preparation are not so important as is the case with catalysis at ordinary pressure with reduced nickel. For instance, in my experiments on the hydrogenation of the aromatic nucleus, which is very difficult to hydrogenate, good results were obtained by using nickel reduced from commercial nickel oxide with hydrogen, the hydrogen (without any purification) being prepared from ordinary commercial zinc and hydrochloric acid. Of course, the purity of a catalyst is always more or less important, but when pressure is used the presence of toxic substances is less harmful.

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[1] Ipatieff, J. Russ. Phys. Chem. Soc., *46*, 302 (1914).

[2] Ipatieff, Ber., *40*, 281 (1907).

[3] See chapter on "Hydrogenation," p. 199.

Finally, my experiments showed that other oxides such as copper oxide might be substituted for nickel oxide [1] in the hydrogenation of the double bond, but in this case, the temperature must be higher than with nickel oxide. Using copper, I was the first to succeed in the catalytic conversion of oleic acid into stearic acid,[2] cinnamic acid into hydrocinnamic acid, and trimethylethylene into isopentane.

Thus, nickel oxide and copper oxide serve equally well for the hydrogenation of double bonds, but for the hydrogenation of the aromatic nucleus it is necessary to use nickel oxide.[3] In the study of the joint action of catalysts,[4] I pointed out the importance of having various oxides simultaneously present in the hydrogenating catalyst. There it was shown that the presence of this or that oxide decreases the temperature of the reaction and changes its course. By the joint action of catalysts, it was possible to directly convert terpenic ketones into hydrocarbons.

My results have been corroborated by the work of Bedford and Erdmann on "Nickel Oxides as Reducing Catalysts for the Addition of Molecular Hydrogen to Unsaturated Fats and Fatty Acids." [5] It should be mentioned that Bedford and Erdmann in analyzing my results on the catalysis of organic compounds, wrongly interpreted some of my experiments and reported a contradiction in my data, but complete agreement was found after comparison of their experimental data with mine.

Evidently, Bedford and Erdmann considered that it was possible to compare experiments on the hydrogenation of the aromatic nucleus with those on the hydrogenation of the double bond of unsaturated compounds. However, if hydrogenation at ordinary pressure in the presence of nickel oxides does not take place with aromatic acids, it cannot be concluded that this reaction is also impossible with unsaturated compounds containing a double bond. The double bond is hydrogenated much more readily than the aromatic nucleus and when nickel is produced from its oxide at 240–260°, double bonds are hydrogenated immediately. Experiments [1] with phenols containing unsaturated side chains confirmed this point.

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[1] Ipatieff, Ber., *42*, 2089 (1909).
[2] *Ibid.*, 2091 (1909).
[3] *Ibid.*, *41*, 1004 (1908).
[4] Refer to "Joint Action of Catalysts," p. 333.
[5] Bedford and Erdmann, J. Russ. Phys. Chem. Soc., *45*, 616 (1913).

Further, Bedford and Erdmann refer to Fokin's experiments (unfortunately they do not give the exact reference) who found that nickel oxide was a good hydrogenation catalyst only at high pressure. Fokin concluded the nickel oxide was useless at ordinary pressure and also up to 10 and 20 atmospheres. Bedford and Erdmann agreed with the findings of Fokin.

The statement of Bedford and Erdmann is not at all in agreement with numerous experiments which I made on the hydrogenation of aromatic and unsaturated compounds. In my experiments, high pressures were employed so that the reaction vessel would hold more material, and in spite of the fact that at the end of the run the hydrogen pressure in the apparatus was as low as 10 to 20 atmospheres, the reaction proceeded to completion. According to experiments made by Fokin and Bedford and Erdmann, the reaction should cease when the pressure reaches about 20 atmospheres but actually this was not observed. My method of hydrogenating under pressure has the advantage that it is possible to carry the reaction to completion and at a more rapid rate than when hydrogenating at ordinary pressure.

Further, Bedford and Erdmann indicate that it was impossible to apply my method of hydrogenating at high temperatures and pressures to fats which decompose readily under these conditions. I used this method for the hydrogenation of oleic acid and obtained stearic acid, even in the presence of copper oxide, a catalyst much less active than nickel oxide and one requiring a higher temperature. If a temperature of 250–260° is required for the hydrogenation of fats in the presence of nickel oxide at ordinary pressure and if fats, according to Bedford's data, can withstand this temperature, then it is impossible to conceive why fats cannot be hydrogenated at this temperature under high pressure. On the contrary, according to my experiments which showed that nickel oxide reduces much more readily under high pressure than at ordinary pressure, it would be anticipated that the hydrogenation of fats in the presence of commercial nickel oxide would take place at a lower temperature under high pressure and give better results than at ordinary pressure, and my experiments have confirmed these expectations.

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[1] Ipatieff, Ber., *46*, 3589 (1913).

Fifty grams of cottonseed oil mixed with 3 g. of nickel oxide was heated in the high pressure apparatus under a hydrogen pressure of 60 atmospheres. From time to time the apparatus was removed from the furnace and shaken. The temperature was only 230°. The solid fat obtained at the end of 4 hours had an iodine number of 11. This experiment was repeated three times. When cottonseed oil was hydrogenated with the same nickel oxide at ordinary pressure in a stream of hydrogen with mechanical stirring, the results were far less favorable than at the same temperature in the high pressure apparatus.

Concerning the rôle of nickel oxide in catalytic phenomena, it is to be noted that Bedford and Erdmann did not pay sufficient attention to my chief purpose in discussing this question in my article "The Rôle of Oxides in the Phenomenon of Catalysis." This investigation was undertaken with the view of finding the most probable hypothesis for explaining oxidation and reduction catalysis. This investigation confirmed the correctness of the hypothesis which I proposed as the first explanation of the catalytic aldehydic decomposition of alcohols. From the theoretical point of view, it was immaterial to me whether the nickel oxide was reduced to metallic nickel or to its lower oxides. All my ideas on catalysis in the presence of nickel oxides were also discussed in detail in the paper "On the Joint Action of Catalysts" which Bedford and Erdmann, for no accountable reason, neglected to cite in spite of the fact that it was published in 1912. In these articles, I [1] described the effect on catalytic reactions of adding various oxides to nickel oxide; but in spite of this Bedford and Erdmann ascribed to themselves [2] priority in the discovery of the action of other metallic oxides upon the activity of nickel oxide.

The test for the presence of reduced metal, using nitric acid of specific gravity 1.4, always gave good results in my experiments with nickel, as well as with other metals and their oxides. Bedford and Erdmann say that I did not indicate that a sub-oxide of nickel also exists which gives an analogous reaction with nitric acid. I would agree with this criticism if they had really proved by their experiments that Moore actually obtained the intermediate sub-oxide of nickel, and that he was not dealing with a mixture of nickel and nickel oxide. Moore's evidence is questionable. As for the significance of the proofs mentioned by Erdmann and Bedford regarding the absence of metallic nickel in the catalyst after hydrogenation, I agree with the conclusions drawn by Meigen and Bartels in their article "On the Solidification of Fats in the Presence of Nickel and Nickel Oxide."[1] The experiments of Bedford and Erdmann did not prove the presence of an intermediate sub-oxide of nickel in the used catalyst, but they did indicate the presence of reduced nickel. The methods proposed by Bedford and Erdmann for proving the presence of this nickel oxide were examined by Meigen and Bartels[1] and found to be unsatisfactory.

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[1] Ipatieff, Ber., *45*, 3205 (1912); J. Russ. Phys. Chem. Soc., *44*, 1675 (1912).

[2] Bedford and Erdmann, J. Russ. Phys. Chem. Soc., *48*, 137 (1913).

Finally, I do not consider that the results of Bedford and Erdmann are in disagreement with mine. According to the data[2] of Bedford and Erdmann, metallic nickel is formed at 190° by the reduction of dry nickel oxide with hydrogen; at 220°, a mixture of nickel and nickel oxide is formed, and at 260° the reduction to the metal is almost complete.

In my experiments[3] at 190°, a considerable amount of reduced nickel was formed. At 220° (Expt. 13), a mixture of nickel and nickel oxide (88.56% of nickel) was obtained; at 280° nickel oxide with a nickel content of 98.1% resulted. I do not see any disagreement in the experimental results.

In conclusion, I will mention certain experiments made in the high pressure apparatus on the hydrogenation of several fatty acids and fats at various temperatures and superatmospheric pressures and also at ordinary pressure. The high pressure apparatus was provided with a special mechanical stirrer which thoroughly mixed its contents. The pressure in the apparatus could be maintained at 70 atmospheres for a considerable length of time. A similar stirrer was also used for the hydrogenation of fats at ordinary pressure in a stream of hydrogen. Numerous experiments showed that this stirrer gave better results than other types of stirrers. Many experiments were made on the hydrogenation of various fats, purified oleic acids, crude oils, cottonseed oil, cod-liver oil, whale oil, linoleic acid, etc. The experiments showed conclusively that whereas hydrogenation of the unpurified linseed oil does not occur at ordinary pressure, it does, however, take place readily under high pressure. The initial pressure of hydrogen in the apparatus varied from 12 to 20 atmospheres, but the reaction proceeded even at lower pressures. Depending upon the duration of the reaction, a product may be obtained with any required proportion of solid fat and iodine number.

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[1] W. Meigen and G. Bartels, Ber. der Naturforsch. Gesellschaft in Freiburg, Band XX; Ber. über die Sitzung, 1913.

[2] Bedford and Erdmann, J. Russ. Phys. Chem. Soc., *45*, 636 (1913).

[3] Refer to my discussion of the rôle of oxides in the phenomena of catalysis, Chapter II, p. 199.

In order to saturate oils with an iodine number of about 100, 1 to 2 hours are required. Two to four hours are required to produce from linseed oil a product melting at 45–48°.

Hydrogenation of fats and oleic acid under pressure begins at 120–130° and in my experiments the temperature was never higher than 170°. Such a temperature is determined, of course, by the properties of the catalyst used in the reaction. When nickel oxide is substituted for specially reduced nickel, the temperature must be increased to 230° which, of course, is unfavorable to the hydrogenation process because at this temperature the unpurified oil may start to decompose, thus retarding the hydrogenation reaction. The preparation of the catalyst requires certain conditions and I had at my disposal catalysts prepared by various methods which gave various speeds of hydrogenation for the same oil.

In Table 74, on page 332, are listed only a few of the experiments on the hydrogenation of various oils.

From the experiments tabulated in the table, the following conclusions may be drawn:

(1) Oils and fats are hydrogenated under superatmospheric pressure at a lower temperature than at ordinary pressure.

(2) With efficient stirring, unpurified oils may be hydrogenated catalytically under pressure. The final pressure in the apparatus was 7 to 8 atmospheres.

(3) By means of nickel, reduced under special conditions, a very high speed of hydrogenation may be obtained. Also, by using mixed catalysts containing promoters (indicated in the table by [a]) very good results may be obtained and the same catalyst may be used several times.

TABLE 74

Oil	Catalyst	Initial Pressure, Atms.	T., °C.	Time, Hrs.	M.P., of Fat, °C.	Iodine Number	Titre	Analysis of Residual Gas
$C_{18}H_{34}O_2$ Oleic Acid Unpurified	Ni	30	152	2.0	61	3.9		
Acid Unpurified	"	20	145	1.5	60.1	4.1		
Acid Unpurified	"	1	185	4.5	53.8	30.7		
Acid Unpurified	NiO	1	260	3.5	35.0			
Acid Unpurified	"	1	250	5.0	38.0			
Cotton Seed Oil	Ni	33	160	2.0		33.0	52.0	
" " "	Ni + Kieselguhr	1	200	2.0	49.4			
Sunflower Seed Oil Unpurified	Ni	33	162	2.0		45.5	52.5	
Oil Unpurified	Ni + Kieselguhr	29	170	2.30		49.0		
Oil Unpurified	Ni [a]	1	215	5.00	57.2			
Linseed Oil Unpurified	Ni + Kieselguhr	34	166	2.5	44	61.3		
Unpurified	Ni	38	168	4.0	48.4			
Unpurified	Ni + Kieselguhr	23.5	168	3.5	52.3			CO_2, 9.2% CO, 4% CH_4, 2.2%
Unpurified	Ni from $Ni(NO_3)_2$	38	162	2.5	49.8			
Unpurified	Ni + Kieselguhr	37	168	4.0	48.4			
Unpurified	Ni + Kieselguhr	20	154	2.0	63.0			CO_2, 0.6% CO, 0.8% CH_4, 4.2%
Unpurified	Ni [a]	35	158	2.5	46.0			
Unpurified	"	37	155	3.5	48.0			
Unpurified	"	20.7	160	2.0	59.0	31.4	50.5	
Linseed Oil Purified	"	1	200	4.0	48.7			
Fish Oil	"	34.0	159	2.3	42.0	48.0	4.0	
" "	"	35.4	159	3.5	43.2	45.4	43.2	
Whale Oil	"	35.6	158	3.0	48.5	20.48	41.5	

[a] Nickel catalysts containing promoters.

CHAPTER VI

JOINT ACTION OF CATALYSTS (PROMOTERS)

INFLUENCE OF FOREIGN SUBSTANCES UPON THE ACTIVITY OF CATALYSTS

In previous investigations [1] it had been shown that the hydrogenation of the olefin bond in aliphatic compounds proceeded very readily under high pressure with copper oxide as catalyst regardless of the structure of the olefin. Experiments also showed that the double bond in the nucleus of hydroaromatic compounds was not hydrogenated with a copper oxide catalyst. The experiments on the addition of hydrogen to tetrahydrobenzene in the presence of reduced copper and copper oxide were made in a high pressure apparatus constructed of phosphor bronze. However, occasionally when an apparatus with an iron tube was substituted for the copper apparatus quite different results were obtained. In this case the double bond present in the nucleus hydrogenated also.

The fact that a copper oxide catalyst produced a different type of hydrogenation depending upon the material of the containing vessel, induced me to initiate a systematic series of experiments in order to determine the extent of this influence.

First, it was necessary to determine whether the hydrogenation of an olefinic double bond with copper oxide proceeded differently in copper than it did in an iron tube. To determine this, numerous experiments were made on the hydrogenation of amylene (trimethylethylene) under various conditions. Previously, it had been shown that amylene hydrogenates [1] quantitatively to *isopentane* in 12 hours at 300° in the presence of copper oxide in an iron apparatus. The product of this hydrogenation was free from olefins as shown by the potassium permanganate test. If no copper oxide was put into the iron tube, the amylene was not hydrogenated in spite of the temperature of 330° and the high hydrogen pressure, but a small part of it was polymerized. If amylene and copper oxide (or reduced copper) were placed under hydrogen pressure in a copper tube instead of in one of iron, hydrogenation took place, but not to completion as it did in an iron tube, in spite of the higher temperature used with the copper tube.

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[1] Ipatieff, Ber., *42*, 2090 (1909).

The results of these experiments are summarized in the following table:

TABLE 75

Metal of Tube	Cat-a-lyst	Hydrogen Pressure, Atms.			T., ° C.	Time, Hrs.	Reaction Product
		Initial	Max.	Final			
Cu	Cu	110	222	80	320	16	66% Unsaturated 33% Saturated
Cu	CuO	110	165	70	320	16	66% Unsaturated 33% Saturated
Cu	Cu	120	195	70	340	28	60% Unsaturated 40% Saturated

The hydrocarbon obtained by hydrogenation in the copper tube consisted of a mixture of isopentane and amylene, boiling at 35–38°; it decolorized potassium permanganate solution and reacted energetically with bromine. To determine the quantity of olefin hydrocarbon remaining unchanged, bromine was added dropwise to 10 g. of the well-cooled reaction product until an orange coloration persisted. Instead of the theoretical amount (23 g. of bromine) only 15 g. of bromine was required. Therefore, the product contained about 66% of amylene. The hydrocarbon which did not react with bromine distilled at 29–31°, did not decolorize potassium permanganate solution, and was identified as *isopentane*.

In the experiments listed in the preceding table, the hydrogenation pressure in the apparatus remained constant for 28 hours at a temperature of 340°. Thus, it might be concluded that the reaction reached a certain state of equilibrium:

$$C_5H_{10} + H_2 \rightleftarrows C_5H_{12}$$

Consequently, the reaction in the presence of reduced copper or copper oxide is reversible. This case is similar to the hydrogenation of cinnamic acid with reduced copper (refer to hydrogenation of acids) in which the addition of hydrogen to cinnamic acid was also found to be a reversible reaction.

Further experiments were made on the hydrogenation of *tetrahydrobenzene* and *methylcyclohexene* in both iron and copper tubes.

Hydrogenation of Tetrahydrobenzene was carried out in the high pressure apparatus with an iron tube using 30 g. of tetrahydrobenzene mixed with 3 g. of copper oxide under 125 atmospheres initial hydrogen pressure. The reaction continued 12 hours at 300°. Pure cyclohexane was obtained which distilled at 80–80.5° and which did not react with nitrating mixture.

Anal. Calcd. for C_6H_{12}: C, 85.7; H, 14.3. Found: C, 85.5; H, 14.0.

Cyclohexane was also obtained when 22 g. of tetrahydrobenzene and 4 g. of *reduced copper* were heated 21 hours at 330° under an initial hydrogen pressure of 120 atmospheres. This cyclohexane did not react with nitrating mixture and it boiled at 80–80.5°.

Hydrogenation of Methyltetrahydrobenzene.—Twenty grams of this hydrocarbon mixed with 3 g. of copper oxide was heated in an iron tube for 7 hours at 330° under an initial hydrogen pressure of 125 atmospheres. According to its properties, the resulting hydrocarbon was pure *methylcyclohexane;* it did not react with nitrating mixture, it boiled at 93–98°, and had a specific gravity of d_{20}, 0.7748.

Anal. Calcd. for C_7H_{14}: C, 85.7; H, 14.3. Found: C, 85.8; H, 14.1.

Hydrogenation of Octahydronaphthalene.—This hydrocarbon (b.p., 188–190°) was prepared from decahydro-beta-naphthol by dehydration with alumina. Fifteen grams of octahydronaphthalene mixed with 3 g. of reduced copper under an initial hydrogen pressure of 110 atmospheres was heated in an iron tube for 18 hours at 300°. The reaction product was a liquid which distilled into the following fractions: (1) 80–83°; (2) 185–190°.

Analysis of the first fraction showed it to be cyclohexane.

Anal. Calcd. for C_5H_{12}: C, 85.7; H, 14.3. Found: C, 85.5; H, 13.4.

Analysis of the second fraction showed it was decahydronaphthalene (decalin).

Anal. Calcd. for $C_{10}H_{18}$: C, 86.9; H, 13.1. Found: C, 87.2; H, 12.9.

Thus, it is seen that the naphthalene nucleus split during the hydrogenation of octahydronaphthalene and that cyclohexane was formed.

These experiments show that the *addition of hydrogen* to a double bond in the aromatic nucleus in the presence of copper oxide occurs as readily as with the olefin linkage of aliphatic compounds, provided that the hydrogenation reaction be brought about in a high pressure apparatus having an iron tube. When a phosphor bronze tube was substituted for the iron tube the results of the hydrogenation of the above-mentioned hydrocarbons were entirely different. The results of these experiments are summarized in the following table.

TABLE 76

Expt. No.	Hydrocarbon, G.	Catalyst, G.	Hydrogen Press., Atms.			T., °C.	Time, Hrs.	d_{20}	Nature of Reaction Product
			Initial	Max.	Final				
1	Tetrahydrobenzene, 21	Copper, 3	98	164	84	340–350	19		B.p., 82–88°, vigorous action with nitrating mixture
2	Tetrahydrobenzene, 25	Copper, 3	108	200	95	350–360	21	0.7900	Vigorous action with nitrating mixture
3	Tetrahydrobenzene, 25	Copper, 3	108	170	87	350	60		Vigorous action with nitrating mixture
4	Tetrahydrobenzene, 25	Copper, 3	108	168	87	350	53		Vigorous action with nitrating mixture.
5	Methylcyclohexene, 20	Copper, 3	101	200	90	353	10	0.7958	Vigorous action with nitrating mixture
6	Tetrahydrobenzene, 3	Copper Iron	110	192	90	350	20		B.p., 80–88°, pure cyclohexane

As shown by the above table, hydrogenation in a copper tube is incomplete and nitrating mixture acts vigorously on the resulting hydrocarbon. When iron filings were placed in the copper tube in addition to the reduced copper catalyst, the hydrogenation continued to completion and pure cyclohexane was obtained.

In order to show how far hydrogenation proceeds in a copper tube, analyses are given of the initial and final products of the following reactions as shown in Table 77 on p. 337.

From these analyses it is to be concluded that a considerable portion of the unsaturated hydrocarbon did not add hydrogen in spite of the fact that the temperature was 20 to 30° higher than

TABLE 77

Expt. No.	Substance Hydrogenated	Analysis			
		Starting Material		Product	
		% C	% H	% C	% H
1	Tetrahydrobenzene	87.8	12.2	87.2	13.0
2	Tetrahydrobenzene	87.4	12.2	86.4	13.6
5	Methylcyclohexene	87.3	12.2	86.6	13.1

that used in the hydrogenation of the same hydrocarbons in an iron tube.

Further hydrogenation experiments were made with *octahydronaphthalene*, *pinene*, and *carvene* in the presence of copper catalysts and the following results were obtained:

TABLE 78

Hydrocarbon	Hydrogen, Press., Atms.			T., °C.	Time, Hrs.	d_{20}	Nature of Reaction Product
	Initial	Max.	Final				
Octahydronaphthalene	109	163	107	348	20	0.9003	B.p., 188–190°; vigorous action with nitrating mixture; isomerization
Pinene	92	153	69	285	28	0.8219	B.p., 167–180°; reaction not complete; resinification
Carvene	108	181		290	28	0.8332	B.p., 170–176°; reaction not complete; resinification

Octahydronaphthalene underwent almost no hydrogenation in a copper tube, as seen from the analysis of the reaction product.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.2; H, 11.8. Found: C, 88.0; H, 12.0.

Pinene and carvene were not hydrogenated completely; that is, they added less than one molecule of hydrogen.

Anal. Calcd. for $C_{10}H_{16}$ (pinene): C, 88.2; H, 11.8. Found: C, 87.6; H, 12.6.

Anal. Calcd. for $C_{10}H_{16}$ (carvene): C, 88.2; H, 11.8. Found: C, 87.5; H, 12.4.

The conclusion from these experiments is that the copper walls of the apparatus produce a marked influence upon the activity of the catalyst, not only as regards the velocity of the reaction, but also as regards its completeness. In some cases there was almost no hydrogenation of the double bond when using a copper tube, although a higher temperature was taken than for hydrogenation in the iron tube. This observed diminution in catalytic activity might be explained either by poisoning (which is probably not important) or it may be assumed that a catalyst develops its complete activity only in the presence of a second substance, e.g., in the presence of iron. On the other hand, it may be that we are dealing with a special kind of combined catalysis which has not been previously investigated.

THE JOINT ACTION OF CATALYSTS (*Continued*); HYDROGENATION OF TERPENES

In order to throw light upon the nature of the joint action of catalysts it was decided to study the hydrogenation of terpenes.

In the following investigations of Ipatieff and Matov an interesting result was obtained by the coöperative effect of two different types of catalysts. As shown by Ipatieff's previous investigations, camphor is converted into borneol in the high pressure apparatus in the presence of nickel oxide at 320–350°, but in order to convert borneol into camphor, the borneol must be heated with alumina in the high pressure apparatus at 350–360°. And it must be mentioned that the latter reaction starts with difficulty and that the final product is liquid camphor mixed with considerable amounts of high boiling material. Likewise, a step-wise catalytic action was observed with fenchone, which was converted into fenchyl alcohol by hydrogen in the presence of nickel oxide. From the latter fenchene was obtained by dehydration over alumina.

The results were entirely different when camphor and a *mixture of nickel oxide and alumina*[1] were heated in the high pressure apparatus under hydrogen pressure. The reaction proceeded rapidly at 200° and after 10 to 12 hours the main product was crystalline isocamphane, melting point, 64–66°.

Thus, at 200°, and probably even lower, under the joint action of the two catalysts, a ketone is easily reduced directly to a saturated hydrocarbon. This may consist in a 3-step reaction, (1) reduction in the presence of the nickel oxide, (2) dehydration in the presence of alumina to give an olefin, and (3) hydrogenation of the olefin. Thus:

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[1] In 1911 I suggested for the first time the use of a mixed nickel alumina catalyst for hydrogenation. In 1924 Zelinsky and Komarewsky, without reference to my work, applied this catalyst to the dehydrogenation of naphthenes. At the present time we have developed several more active catalysts for dehydrogenation.

$$(1)\quad C_{10}H_{16}O + H_2 \rightarrow C_{10}H_{18}O$$

$$(2)\quad C_{10}H_{18}O \rightarrow C_{10}H_{16} + H_2O$$

$$(3)\quad C_{10}H_{16} + H_2 \rightarrow C_{10}H_{18}$$

If it is assumed that instead of these three reactions there is direct reduction of the ketone to the saturated hydrocarbon, we have no proof that the alumina might be considered as an inductor for a conjugated reaction. Certainly, the decided drop in the temperature of the reduction can be ascribed to the presence of alumina because with nickel oxide alone, even 400° is not sufficient to produce isocamphane from camphor, as shown by special experiments. This reaction in the presence of two catalysts might rightfully be called a hydrolytic reduction.

A similar reaction proceeds when hydrogen is permitted to act upon borneol at 220° in the presence of nickel oxide and alumina, crystalline isocamphene being obtained. When copper oxide is added to alumina instead of nickel oxide, the action of these two catalysts upon the alcohol in the presence of hydrogen is entirely different. In this case, in spite of the ability of copper oxide to act as a reduction catalyst, no bicyclic saturated hydrocarbon is formed from borneol or isoborneol, but camphene is the sole product. Depending upon the temperature used, only liquid or liquid and solid hydrocarbons are obtained from borneol.

As an explanation of the joint action of catalysts,[1] it is possible to assume that a labile complex is formed between the two catalysts, such as nickel oxide—aluminum oxide. This complex then decomposes and reforms *in statu nascendi*. The reformed catalyst is more active and the catalytic reaction proceeds at a much lower temperature.

In the reduction of camphor, nickel oxide serves as the primary catalyst because the formation of borneol is necessary before the second catalyst, alumina, may cause the production of camphene. In the reduction of borneol, alumina serves as the primary catalyst for the formation of camphene, which is then reduced under the influence of the secondary catalyst, nickel oxide. If copper oxide and alumina are used instead of nickel oxide and alumina, then it may be assumed that a complex consisting of alumina and cupric oxide is formed.

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[1] See chapter "Theoretical Principles of Catalytic Reactions."

In spite of the fact that this reaction is carried out in the presence of hydrogen, the camphene formed under the influence of alumina is not reduced because the reaction temperature of 200° is too low for the hydrogenation of the double bond in the presence of copper oxide or of reduced copper catalyst. The acceleration of the dehydration of borneol might be ascribed to the influence of the concurrent reduction of copper oxide to metallic copper.

If the action of inorganic catalysts upon organic compounds is explained in this manner, it must still be noted that a hypothesis of this kind is not different from the conceptions advanced to explain the acceleration of the oxidation of ferrous compounds by hydrogen peroxide, as well as for the splitting of activated oxygen from the peroxide under the influence of certain salts. These salts cause acceleration of the oxidation not because they absorb oxygen from the air, but because, as shown by experiments of Melikov and Pissarschevsky, they form labile complexes with peroxides which split off activated oxygen more readily than does the peroxide alone. This same hypothesis has been developed also by Bach as an explanation of the hydrolytic reduction and oxidation processes which occur in the metabolism of living matter.

Hydrogenation of Terpenes [1]

The study of the hydrogenation of terpenes was selected as a suitable approach to an understanding of the mechanism of promoter action.

Preparation of Fenchane and Fenchone.—In order to prepare fenchane from fenchone the latter was converted into the alcohol fenchanol by hydrogenation and the water was split from this alcohol by the method of Ipatieff in the presence of alumina to give the unsaturated hydrocarbon fenchene which was hydrogenated to fenchane.

If Semmler's formula is assumed for the structure of fenchone, these transformations may be expressed by the following formulas:

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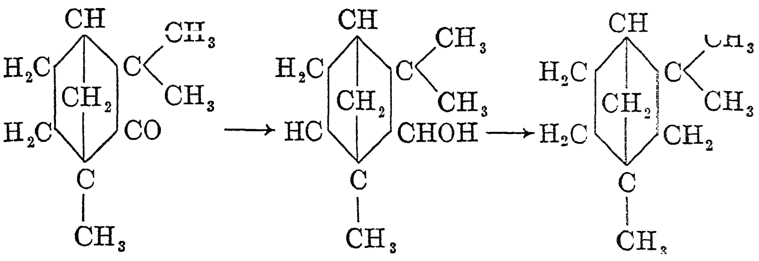
[1] Ipatieff and Matov, J. Russ. Phys. Chem. Soc., *44*, 1695 (1912); Ber., *45*, 3205 (1912).



The conversion of fenchone into an excellent yield of the alcohol takes place readily on catalytic hydrogenation under pressure in the presence of nickel oxide. The fenchone (obtained from Kahlbaum) had the following properties: boiling point, 187°; $(\alpha)_D$, 58.92°; d_{20}, 0.9463. It was heated at 240° in the high pressure apparatus for 20 hours under an initial hydrogen pressure of 110 atmospheres. After the first distillation, 90% of fenchanol was obtained with the following physical constants: boiling point, 196° (752 mm.); d_{20}, 0.9554; $(\alpha)_D$, 0°.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.9; H, 11.7. Found: C, 77.5; H, 11.6.

The change from fenchanol to fenchene by splitting off water by the action of alumina proceeded with difficulty. Also, the yield of the unsaturated hydrocarbon was very small in spite of the use of temperatures ranging from 260 to 355°. At lower temperatures, much of the alcohol was unchanged, while at higher temperatures condensation products and considerable thick resin resulted. Isomerization is a possible explanation of the difficulty in dehydrating fenchanol if Semmler's formula is assumed. The fenchene obtained in small amounts had the following constants: boiling point, 150–160° (745.5 mm.); d_{20}, 0.8397; n_{20}, 1.44909.

Anal. Calcd. for $C_{10}H_{18}$: C, 87.0; H, 13.0 Found: C, 86.9; H, 12.8.

Because the yield of fenchene was small an attempt was made to prepare it by way of its bromide, but here also the results were disappointing. Accordingly, trial was made of the direct conversion of fenchanol into fenchane by the joint catalytic action of nickel oxide and aluminum oxide.

Forty grams of fenchanol and 4 g. of a mixed catalyst (2.5 g. nickel oxide and 1.5 g. alumina) were taken and 110 atmospheres of hydrogen pressure was applied. The reaction proceeded at 215°

and was finished after 12 to 14 hours when the pressure in the apparatus remained constant. Distillation of the product (93 g.) gave the following fractions: (1) 160–167° (73 g.); (2) 167–180° (16 g.); (3) above 180° (4 g.).

The first two fractions did not decolorize potassium permanganate solution. The first fraction did not react with nitrating mixture and the second became only slightly warm by the action of this reagent, a result indicating the presence of a small amount of unchanged fenchanol. Experiments showed that if this fraction is subjected to a second hydrogenation under the action of the mixed catalyst the product has the same properties as those of the first fraction. By repeated fractional distillation of the first fraction, a product was separated which boiled at 162–163° (737.8 mm.) and constituted the chief component of the first fraction. Its physical constants were as follows: d_{17}, 0.8766; d_{20}, 0.8733; n_{17}, 1.45409; $(\alpha)_D$, $+19.83°$.

Anal. Calcd. for $C_{10}H_{18}$: C, 87.0; H, 13.0. Found: C, 87.2; H, 12.7.

According to these data, fenchane appears as the chief product of the reaction. In its properties, it approaches more closely the fenchane formed by the reduction of fenchene by Zelinski rather than the one of Kijner,[1] obtained from fenchone by transition through fenchyliden-hydrazine.

Kijner's fenchane had the physical constants: b.p., 151.5° (763.5 mm.); d_{20}, 0.8323; n_{20}, 1.4463; $(\alpha)_D$, $-16.53°$.

The properties of Zelinski's fenchane were: b.p., 162.5–163.5° (751 mm.); d_{20}, 0.8550; n_{20}, 1.4560; $(\alpha)_D$, $+8.16°$.

Preparation of Isocamphane from Camphene.—Before describing experiments for the preparation of isocamphane from camphor and from borneol, data will be presented on the preparation of isocamphane by hydrogenation of commercial camphene under high pressure in the presence of nickel oxide.

Camphene from Kahlbaum had the following properties: m.p., 48.5°; $(\alpha)_D$, 0°; b.p., 160–165° (161 mm.).

The hydrogenation of camphene proceeded best at 240° and required from 12 to 15 hours for completion. The reaction product, a solid with a camphor-like odor which dissolved easily in ethyl ether, ligroin, methyl, and ethyl alcohol, reacted neither with potassium permanganate solution nor with nitrating mixture.

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[1] Kijner, J. Russ. Phys. Chem. Soc., *43*, 592 (1911).

The hydrocarbon obtained distilled almost completely at 160–166°. After purification by distillation and crystallization from absolute alcohol, a final product was separated which had the following physical constants: b.p., 162.5–163.5° (758 mm.); m.p., 55.5–57.0°; $(\alpha)_D$, 0°; d_{19}, 0.8457.

Anal. Calcd. for $C_{10}H_{18}$: C, 87.0; H, 13.0. Found: C, 87.3; H, 12.6.

According to the analysis and the physical constants, the product was isocamphane which is slightly different from isocamphane obtained by Lipp [1] by hydrogenating pure inactive camphene in accordance with the method of Sabatier and Senderens who hydrogenated other camphenes in the presence of platinum black. Lipp obtained both the liquid and the solid isocamphane. Further, it is evident that liquid isocamphane was obtained by the hydrogenation of liquid camphene prepared by dehydrogenating borneol in the presence of a mixed catalyst.

Preparation of Isocamphane from Borneol.—When borneol was subjected to dehydration by means of alumina, the reaction proceeded rather slowly at 350–360° producing large amounts of tarry materials and only a small yield of the liquid camphene. This is similar to the case of fenchanol; in order to pass more conveniently from borneol to isocamphane, use was made of the joint action of the catalysts nickel oxide and alumina.

The borneol taken for hydrogenation had the following properties: m.p., 208–210°; b.p., 215°; $(\alpha)_D$, +30.21°. Forty grams of borneol, 2.5 g. nickel oxide, and 2 g. alumina were heated together in the high pressure apparatus at 215–220° for 10 to 12 hours under 110 atmospheres initial hydrogen pressure. The reaction product was a solid weighing 81 g., of which 78 g. distilled at 164–167°. This substance, which had a faint camphor-like odor, reacted neither with potassium permanganate solution nor with nitrating mixture. No resinous products were obtained.

After distillation and crystallization from alcohol, the product had the following properties which corresponded to those of isocamphane: m.p., 63.0–64.5°; b.p., 164° (757 mm.); d_{70}, 0.84157; $(\alpha)_D$, −8.50°.

Anal. Calcd. for $C_{10}H_{18}$: C, 87.0; H, 13.0. Found: C, 87.2; H, 13.0.

When hydrogenation was attempted at 200° instead of at 220°

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[1] Lipp, Ann., *382*, 265–305 (1911).

the reaction proceeded very slowly and a large amount of borneol remained unchanged in spite of continued heating.

Preparation of Isocamphane from Isoborneol.—Isoborneol, heated with alumina alone at 350–360° yielded crystalline camphene, but, because of the high temperature, a considerable quantity of condensation products was also formed. Isocamphane was obtained directly from isoborneol by the joint action of nickel oxide and alumina at 215°.

The isoborneol used for the hydrogenation had the following properties: b.p., 211°; m.p., 219°; $(\alpha)_D$, −1.82°. Under 100 atmospheres initial hydrogen pressure 40 g. isoborneol, 2.5 g. nickel oxide, and 1.5 g. alumina were heated in the high pressure apparatus at 215° for 10 to 12 hours.

The resulting solid product did not react with potassium permanganate solution nor with nitrating mixture. After distillation and recrystallization from ethyl alcohol, the product obtained had properties and analysis corresponding to those of isocamphane: b.p., 164–164.5° (756.1 mm.); m.p., 62.5–64.0°; d_{70}, 0.84293; $(\alpha)_D$, −2.81°.

Preparation of Isocamphane from Camphor.—The joint action of catalysts which are effective in reduction and dehydration reactions, respectively, facilitates the transition from alcohols to the saturated cyclic hydrocarbons. The application of this method to the cyclic ketones, carvomenthone and camphor, also accomplished a satisfactory reduction of the ketone group to form saturated hydrocarbons. This reaction proceeded at a lower temperature with these ketones than with the corresponding alcohols.

By heating 30 g. of carvomenthone with hydrogen at 220° for 12 hours in the high pressure apparatus in the presence of 2.5 g. nickel oxide and 1.5 g. alumina, a liquid was obtained with a boiling point of 165–168°. According to its properties, this product was pure menthane.

Camphor with the following properties was taken for the experiments: b.p., 203.5° (743.2 mm.); m.p., 174.5–176.0° $(\alpha)_D$, +33.20°.

For successful hydrogenation of camphor, the temperature should not be raised rapidly and should not exceed 205°, otherwise the camphor will sublime and collect in the upper colder parts of the tube and consequently escape reduction.

Thirty grams of camphor, 3 g. of nickel oxide, and 1.5 g. of alumina were heated at 200° for 24 hours under hydrogen pressure. The solid product did not react with potassium permanganate solution, nor with nitrating mixture. After distillation and recrystallization from ethyl alcohol, its properties designated it as isocamphane: b.p., 164–165° (757 mm.); m.p., 64.5–65.6°; d_{70}, 0.8462; $(\alpha)_D$, −3.95°.

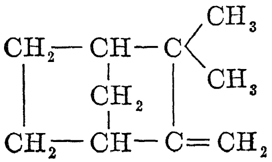
Anal. Calcd. for $C_{10}H_{18}$: C, 87.0; H, 13.0. Found: C, 87.1; H, 13.0.

TABLE 79

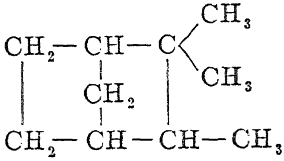
PHYSICAL CONSTANTS OF ISOCAMPHANES

ISOCAMPHANE PREPARED FROM	BOILING POINT [°C. @ (mm.)]		MELTING POINT, °C.	d_{70}	$(\alpha)^{17}_D$
Camphene	162.5–163.5	(761)	55.5–57.0	0.8457	0.00
Borneol	164.0	(757)	63.0–64.5	0.8416	−8.50
Isoborneol	164.0–164.5	(756)	62.5–64.0	0.8429	−2.81
Camphor	164.0–165.0	(757)	64.5–65.5	0.8462	−3.95

The preceding table shows that the properties of the isocamphanes are closely related to one another although different starting materials were used for the preparation (by the joint action of catalysts). If Wagner's formula for isocamphene is assumed, then the structure of isocamphane may be represented by the following formula:



Isocamphene



Isocamphane

The direct preparation of isocamphane from alcohols and camphor under the joint action of catalysts is interesting not only from the viewpoint of catalysis, but it offers the possibility of establishing certain assumptions concerning the structure of certain camphor derivatives. According to the experiments of Lipp and Ipatieff the existence of a new isocamphane is certain; it is an isomer of camphane having a melting point of 57°. The latter was prepared first by Kechler and Schnitzer [1] by removal of chlorine from borneol chloride with metallic sodium in boiling benzene solution. Later, Kijner [1] obtained it by catalytic decomposition of camphilidene hydrazine. The so-called isohydrocamphane (m.p., 85°) obtained by Semmler by heating isoborneol with zinc dust under pressure at 220° is probably not a homogeneous product.

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[1] Kechler and Schnitzer, Ber., *13*, 2236 (1880).

According to the methods of preparation, camphane possesses a camphor ring (Bredt) and an asymmetrical structure. Isocamphane, according to its method of preparation and its formation, must correspond to the complete isomerization of the initial products. This latter circumstance led to the assumption that the structural formulas of borneol and isoborneol are identical and that these alcohols represent space-isomers.

In addition, it must be noted that the melting point of isocamphane obtained from camphene is 6° lower than that of isocamphane obtained from other substances. Up to the present time, there are no data to serve as bases for a discussion of this question, though it is still interesting to investigate the individual isocamphanes obtained and to determine their relation to various camphenes.

Preparation of Camphene from Borneol—If a mixture of alumina and copper oxide instead of alumina and nickel oxide is used for treating terpenic alcohols the products are not saturated but unsaturated hydrocarbons. The temperature for the catalytic dehydration of alcohols by the joint action of alumina and copper oxide falls to a considerable extent [2] (from 360 to 220°). As a result of the use of this low temperature, no hydrogenation of the double bond occurs and the hydrocarbon remains unsaturated.

Thirty grams of borneol, 2 g. of alumina, and 1 g. of copper oxide were heated for 14 to 16 hours at 200–220° in the high pressure apparatus under 50 atmospheres initial hydrogen pressure. A mixture of solid and liquid camphene (about 80% of the total) appeared as the reaction product. Practically no resinification was observed.

After distillation and recrystallization from alcohol the solid camphene had the following properties: b.p., 156–159° (763 mm.); m.p., 60–62.5°; d_{70}, 0.85075.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.2; H, 11.8. Found: C, 87.7; H, 12.2.

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[1] Kijner, J. Russ. Phys. Chem. Soc., *43*, 583 (1911).

[2] For an explanation, see below.

The high melting point of the resulting camphene leads one to assume the presence of an isomer, probably bornylene,[1] but as yet this assumption has no experimental proof. After distillation, the liquid camphene had the following properties: b.p., 155–160° (763 mm.); d_{16}, 0.8688; n_D^{16}, 1.45819; $(\alpha)_D$, +1.61°.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.2; H, 11.8. Found: C, 88.0; H, 11.9.

Except in boiling point, this liquid camphene is similar to the pinolene of Aschan;[2] b.p., 148°; d_{20}, 0.8599; $(\alpha)_D$, 1.63°; n_D^{20}, 1.45768. On the addition of dry hydrogen chloride in alcoholic solution, Ipatieff's liquid camphene gave a chloride melting at 140°, while the chloride of Aschan's pinolene melted at 38°.

When liquid camphene is hydrogenated in the presence of nickel oxide, it adds two atoms of hydrogen per molecule of hydrocarbon and is converted into a liquid isocamphane having the following constants: b.p., 160–165°; d_{18}, 0.85204; n_D^{18}, 1.45009; $(\alpha)_D$, 0°. This liquid isocamphane is identical with the liquid hydrocarbon which Lipp obtained from commercial camphene by hydrogenation according to the method of Sabatier. Lipp assumed that this product was formed from Aschan's pinolene contained in commercial camphene, but our experiments showed his assumption to be incorrect.

Preparation of Camphene from Isoborneol.—On heating a mixture of isoborneol, alumina, and copper oxide at 200° for 20 hours (in the high pressure apparatus) under an initial hydrogen pressure of 65 atmospheres, a solid camphene only was obtained with the following properties: b.p., 162–167° (766 mm.); m.p., 53.5°; d_{70}, 0.85092; n_D^{60}, 1.44244.

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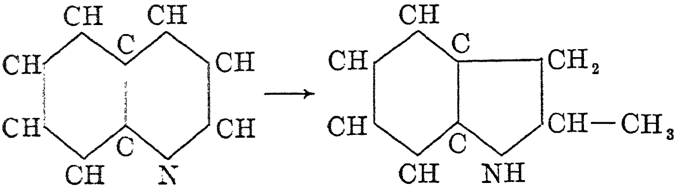
[1] Wagner, Ber., *32*, 2312 (1899).

[2] Aschan, Ber., *40*, 2750 (1907).

CHAPTER VII

HYDROGENATION OF AROMATIC AMINES[1] AND METALLO-ORGANIC COMPOUNDS

In the reduction of aromatic amines in the presence of reduced nickel at ordinary pressure,[2] side reactions take place which considerably decrease the yield of the chief reaction product. The side reactions are especially disturbing in the hydrogenation of *diphenylamine*, which gives very little of its normal reduction product, dicyclohexylamine. According to experiments of Padoa and Carughi,[3] *quinoline* cannot be hydrogenated under these conditions. In the presence of reduced nickel and hydrogen at ordinary pressure, quinoline is converted into *methylindol*.



However, when aromatic amines and quinoline are hydrogenated according to Ipatieff's method under pressure in the presence of nickel oxide, the reaction proceeds rapidly to give a good yield of the main hydrogenation product. The hydrogenation of aniline, diphenylamine, and quinoline are described below as examples of the hydrogenation of organic bases.

Hydrogenation of Aniline.—Thirty grams of aniline and 2 g. of nickel oxide were heated in the high pressure apparatus under hydrogen pressure (115–120 atmospheres). After heating at 220–230° for 40 to 50 hours (without stirring), the experiment was discontinued since the pressure no longer fell, and the product of the reaction was distilled. The yield of the normal reaction product, cyclohexylamine, was 50%, which is considerably more than that obtained according to the method of Sabatier. When the reaction mixture was well stirred, hydrogenation proceeded much more rapidly and a larger yield of the major product resulted. Among other reaction products were unchanged *aniline* and *dicyclohexylamine.* The gas remaining in the apparatus was pure hydrogen.

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[1] Ipatieff, Ber., *41*, 991 (1908).

[2] Sabatier and Senderens, Compt. rend., *138*, 457, 1257 (1904).

[3] Padoa and Carughi, Atti. accad. Lincei., (5), *15*, 113 (1906).

Hydrogenation of Diphenylamine.—A mixture of 25 g. of diphenylamine and 2 g. of nickel oxide was heated in the high pressure apparatus under an initial hydrogen pressure of 125 atmospheres. After heating for 36 hours at 225–230° the pressure remained constant. The liquid reaction product consisted chiefly of a fraction boiling at 254–255° which contained pure *dicyclohexylamine,* $C_6H_{11}—NH—C_6H_{11}$.

Anal. Calcd. for $C_{12}H_{23}N$: C, 79.6; H, 12.7; N, 7.7. Found: C, 80.0; H, 13.1; N, 7.8.

Dicyclohexylamine prepared by this method possessed all the properties of a secondary aliphatic amine. It solidified to a crystalline mass on cooling in an ice-salt freezing mixture, and reacted with hydrochloric acid to give a crystalline salt which precipitated from aqueous solution in the form of needles. Besides this chief product, a small amount of *cyclohexylamine* (b.p., 275°) was obtained as a decomposition product of dicyclohexylamine.

$$2C_6H_{11}—NH—C_6H_{11} + H_2 \rightarrow C_6H_{11}—NH_2 + C_6H_{12}$$

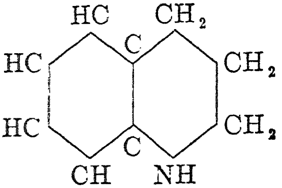
Because of the excellent yield of dicyclohexylamine, this hydrogenation method is recommended for its preparation.

Hydrogenation of Quinoline.—A mixture of 20 g. of quinoline and 2 g. of nickel oxide under an initial hydrogen pressure of 110 atmospheres was heated at 240° for 12 hours without stirring. At the end of the reaction, that is, when the pressure became constant, a solid product was obtained by ether extraction which distilled completely at 207–210° (760 mm.). On standing it formed a crystalline mass which melted at 45.5°. Analysis of this product showed it to be *decahydroquinoline.*

Anal. Calcd. for $C_9H_{17}N$: C, 77.7; H, 12.2; N, 10.1. Found: C, 77.2; H, 12.4; N, 10.1.

Decahydroquinoline is obtained in needle-shaped crystals having an odor suggestive of amines. It is deliquescent, fumes in air, and absorbs carbonic acid energetically with the formation of the corresponding salt. Its hydrochloride is soluble in water and alcohol and crystallizes well from the latter.

When the hydrogenation of quinoline is not continued to the end, there is formed, in addition to decahydroquinoline, a liquid boiling at 250–255° which consists chiefly of *tetrahydroquinoline.*



Anal. Calcd. for $C_9H_{11}N$: N, 10.5. Found: N, 10.4, 10.5.

On mixing hot solutions of tetrahydroquinoline and picric acid, the picrate of tetrahydroquinoline was obtained in the form of golden needles.

Anal. Calcd. for $C_{15}H_{14}N_4O_7$: N, 15.5. Found: N, 14.5, 14.6.

Thus this experiment shows that it is easy to hydrogenate quinoline by the Ipatieff method so as to obtain various degrees of hydrogenation. Of course, this method may be applied also to the preparation of hydrogenation products of other organic bases.

HYDROGENATION OF METALLO-ORGANIC COMPOUNDS[1]

In the course of my investigations on the displacement of metals from aqueous solutions of their salts by hydrogen under high pressure,[2] it was established that the reaction proceeds according to the equation:

$$\text{Met}\,(X)_y + y/2H_2 \rightarrow \text{Met} + yHX$$

However, this reaction does not always go to the end. In many cases, water and the eliminated acid act upon the displaced metal so as to establish an equilibrium between the metal, its oxide, and the acid. A special case of such an equilibrium was found in my experiments together with Ipatieff, Jr., on solutions of lead nitrate. The quantities of crystalline basic salts, lead oxide, and metallic lead in the product depended upon the initial pressure of the hydrogen.

For further study of the theory of the displacement of metals by hydrogen, it was interesting to investigate the action of hydrogen upon metallo-organic compounds in the absence of water.

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[1] Ipatieff, Razuvaev, and Bogdanow, Ber., *63*, 335 (1930).

[2] Ipatieff and Werhovsky, Ber., *42* (1909); *56*, 1663 (1923); *59*, 1412 (1926); *60*, 1952 (1927); *61*, 624 (1928); *62*, 386 (1929).

For this purpose, organic lead compounds were chosen. Among the compounds selected for study (see following table) were tetraphenyl,[1] tetramethyl, and tetraethyl lead, which were synthesized from lead chloride and RMgX and which had been studied previously by Güttner and Krause.[2] The present experiments were carried out principally with lead tetraphenyl since this compound is very stable and readily obtainable.

TABLE 80

PREPARATION AND PROPERTIES OF ORGANIC LEAD COMPOUNDS USED IN HYDROGENATION EXPERIMENTS

COMPOUND	PROPERTIES OF LEAD COMPOUNDS				PREPARED IN ETHER SOLUTION FROM $PbCl_2$ AND
	B.P., °C.	M.P., °C.	Analysis, % Pb		
			Calcd.	Found	
$Pb(C_6H_5)_4$		224–226	40.2	39.7[a]	C_6H_5MgBr
$Pb(CH_3)_4$	109–111		77.5	77.4	CH_3MgI
$Pb(C_2H_5)_4$	88–90 at 18 mm.		64.1	63.7	C_2H_5MgBr

[a] This analysis was made according to the method of Polis (treatment with sulphuric acid and potassium permanganate), Ber., *20*, 717 (1887).

The action of hydrogen under pressure and at high temperature upon the compounds mentioned above caused a displacement of lead and the formation of a hydrocarbon, according to the equation:

$$PbR_4 + 2H_2 \rightarrow Pb + 4RH$$

In the present case, this hydrogenation reaction of metallo-organic compounds was not reversible and under certain conditions which differed for various compounds, the displacement of the metal proceeded to completion. The temperature, the initial hydrogen pressure, and the duration of the experiment influenced the amount of metal precipitated. A study of these influences was carried out chiefly with lead tetraphenyl with the following conditions kept constant: concentration (0.001 mole per 25 cc. of solvent); initial hydrogen pressure (60 atmospheres), duration of the experiment (24 hours).

Under these conditions, separation of metal from lead tetraphenyl in benzene solution started at approximately 150°. At 250° the separation of the metal was quantitative, but the main reaction occurred within the temperature interval of 175 to 225°.

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[1] Pfeiffer and Truskier, Ber., *37*, 1126 (1904).

[2] Güttner and Krause, Ber., *61*, 624 (1928); Ber., *49*, 1420 (1916).

From *lead tetraethyl* under similar conditions 15% of the lead separated as free metal at 100°; complete separation was obtained at 225°. *Lead tetramethyl* commenced to decompose at 125° and separation of metal was quantitative at approximately 250°.

The experimental results are summarized in Table 81 and Fig. 27 in which the amounts of metal displaced from lead tetraphenyl and lead tetraethyl are expressed in percentage. The results given for lead tetramethyl were not based upon a direct determination of the metal separated, but were established by determining the quantity of metallo-compound which did not react.

TABLE 81

INFLUENCE OF TEMPERATURE UPON THE DISPLACEMENT OF LEAD IN BENZENE SOLUTION

T., °C.	PERCENTAGE OF LEAD SEPARATED FROM			SUBSTANCE UNDECOMPOSED, %		
	$Pb(C_6H_5)_4$	$Pb(C_2H_5)_4$	$Pb(CH_3)_4$	$Pb(C_6H_5)_4$	$Pb(C_2H_5)_4$	$Pb(CH_3)_4$
100		15.09				
125		18.10		98.0		
150	3.4	28.2	8.5			91.5
175	7.3	50.4	55.5	89.8		44.4
200	55.7	85.6	89.0	41.8	14.0	11.0
225	92.2	99.0	94.6		Traces	5.4
250	99.6		100.0	Traces		Traces

The experiments on lead tetraphenyl with hydrogen under pressure were made in the following manner: Into a glass tube 1.5 cc. in diameter and about 50 cm. in length were placed 0.001 mole of the substance (0.5154 g.) and 25 cc. of solvent. The tube was covered with a glass hood and placed in the high pressure apparatus into which 5 cc. of the solvent was poured. Hydrogen was then pumped in, and the apparatus was closed and heated. At the end of the reaction, the product was treated in the glass tube with hot benzene to dissolve the lead tetraphenyl which had not reacted. This benzene solution was evaporated to dryness on a water bath and the lead content in the residue was determined by the Polis [1] method.

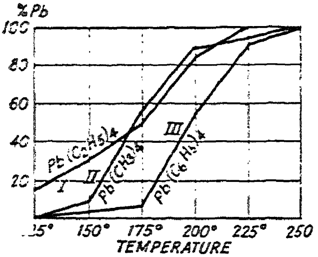

FIG. 27

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[1] Polis, Ber., *20*, 717 (1887).

A considerable quantity of the lead displaced from the metallo-organic compound precipitated on the walls of the tube in the form of a mirror which was dissolved in nitric acid and determined as lead sulphate.

Because of their toxic properties, lead tetramethyl and lead tetraethyl were not weighed but the necessary amounts were measured volumetrically by an accurate pipette, 0.14 cc. lead tetramethyl (*d*, 1.9951) or 0.20 cc. lead tetraethyl (*d*, 1.6591) corresponding to 0.001 mole.

The method of analysis of lead tetramethyl and tetraethyl was the same as that of Krause [1] except for certain changes. A solution of the compound in benzene was treated in the cold with a 10% solution of bromine in benzene. The reaction product was evaporated to dryness on a water bath, the residue boiled for several minutes with absolute alcohol, cooled, filtered through a Gooch crucible, washed sparingly with cold alcohol, and the lead bromide remaining on the Gooch was weighed.

The volatility of lead tetramethyl made quantitative determinations according to the method of Krause difficult. The amount of lead displaced could not be determined quantitatively because the compound volatilized and decomposed on the walls of the apparatus from which it was impossible to remove the lead. In order to determine the amount of the compound remaining undecomposed, the apparatus and the tube were washed with benzene; the hydrogen released from the apparatus was passed through a solution of bromine in benzene, and the amount of lead bromide was determined in the resulting solution.

As seen from Table 81, the volatility of lead tetramethyl at low temperatures is very great; at higher temperatures, there was a decrease in the difference between the metal displaced and the compound remaining undecomposed. To obtain more information on the process of decomposition, an experiment was made using 1 cc. of the substance, corresponding to 0.0075 mole. The experiment was continued for 48 hours at 250° at the end of which time the pressure was 25 atmospheres (initial 60 atmospheres). At the end of the experiment, analysis of the gases remaining (7.51 liters) showed the presence of 6.7% methane. Therefore, 557 cc. or 0.025 mole of methane was formed; theory required 0.030 mole.

Analysis of the displaced metal and of the compound remaining undecomposed indicated that lead tetraethyl is non-volatile, similar to lead tetraphenyl.

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[1] Krause, Ber., *49*, 1130 (1916).

Effect of Temperature.—Comparing the results of the displacement of metal from the compounds indicated, it is to be concluded that lead tetramethyl and lead tetraethyl are closely related, and that the splitting of the radicals and their simultaneous hydrogenation proceed with comparative ease. Lead tetraphenyl is more stable to this decomposition reaction. These three lead compounds when arranged in their order of increasing stability to the action of hydrogen, form the series: tetraethyl, tetramethyl, and tetraphenyl. This result is slightly different from the conclusions of Güttner and Krause concerning the stability of the bonds between the metal and the radicals. When lead compounds containing various alkyl radicals were treated with bromine, these investigators[1] found that the group with the smaller molecular weight was split off, that is, the strength of the bond between the metal and the radical increased with increase in the molecular weight of the radical. In the aromatic series,[2] on the contrary, the heavier radicals were split off first. The aliphatic groups are in general bound more securely than the aromatic, but the *cyclohexyl group* has the strongest bond.

In order to establish the fact that the separation of lead occurred under the influence of hydrogen and was not due to pyrogenetic decomposition of the initial substance, blank runs were made under the same conditions as described above but in the absence of hydrogen and at 200°. It was found that lead tetraphenyl and lead tetramethyl remained practically unchanged, but that lead tetraethyl decomposed partially, forming a white precipitate containing 11% of lead. In the presence of hydrogen, as seen from Table 81, an 86% separation of metallic lead took place at 200°, but in the absence of hydrogen, metallic lead was not separated and the amount of decomposition was only 11%. This agrees with the data of Güttner and Krause who found that the alkyl derivatives of lead decompose in sunlight with the formation of white and brown precipitates, but they never observed the separation of metallic lead.

Effect of Pressure.—The influence of pressure was studied in solutions containing 0.001 mole of lead tetraphenyl in 25 cc. of benzene. Pressures from 5 to 150 atmospheres were included in the study. The temperature was maintained at 200° and the duration of the experiments was 24 hours. The results of the experiments are summarized in Table 82 (Fig. 28).

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[1] Güttner and Krause, Ber., *50*, 202 (1917).

[2] Güttner and Krause, *58*, 427 (1925).

TABLE 82

Initial Hydrogen Press., Atms.	Lead Displaced, %	Lead Tetraphenyl Undecomposed, %
5	11.6	85.2
15	19.5	80.4
25	28.6	67.7
60	55.3	41.8
100	55.7	41.5
125	55.7	42.6
150	60.0	

At the beginning of the experiment under low pressure, an increase in pressure markedly increased the amount of metal displaced; but under higher pressure, the effect was less. This fact is in complete agreement with the results of all my experiments on the displacement of metals from aqueous solutions of their salts.

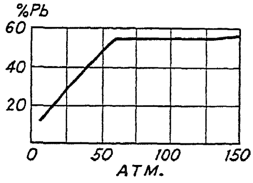

Fig. 28

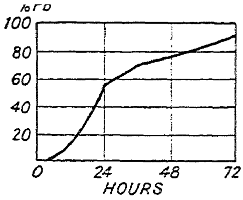

Fig. 29

Effect of Time.—The influence of time was studied in benzene solution under the established standard conditions mentioned above. The results are summarized in Table 83 (Fig. 29).

TABLE 83

Duration of Experiment, Hrs.	Lead Displaced, %	Lead Tetraphenyl Undecomposed, %
6	5.2	93.4
12	13.9	93.6
18	30.1	67.1
24	55.3	41.8
36	70.6	24.4
48	76.8	20.5
72	92.4	5.6

From the curve it is obvious that the greater part of the displacement of lead occurred during the first 24 hours and that the effect of time was not so pronounced when the experiment was prolonged.

Comparing experiments heated for 72 hours under 60 atmospheres initial pressure with those conducted for 24 hours under an initial pressure of 150 atmospheres, it is to be concluded that a combination of all the factors is necessary for an energetic displacement. Increase in only one factor does not produce a marked increase in the amount of metal separated from the metallo-organic compounds. It is obvious that by changing one factor at a time that the effect of each factor can be determined separately.

Effect of Solvent and Temperature.—The effect of temperature upon the amount of metal separated was studied in the presence of a number of solvents. The results are summarized in Table 84.

TABLE 84

EFFECT OF SOLVENT ON THE DISPLACEMENT OF LEAD FROM LEAD TETRAPHENYL BY HYDROGEN

T., °C.	BENZENE		ACETONE	ALCOHOL	LIGROIN[a]
	Displaced, %	Undecomposed, %	Displaced, %	Displaced, %	Displaced, %
125		98.0			
150	3.5				
175	7.3	89.8			
200	55.3	41.8	78.9	50.0	11.1
225	92.2		91.9	90.9	
250	99.6	Traces	97.1	100.1	100.0

[a] Purified from aromatic and unsaturated hydrocarbons.

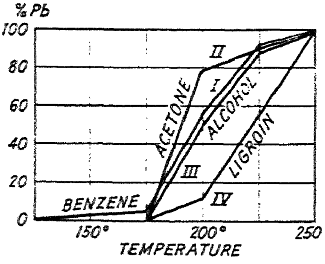

FIG. 30

These data show that the solvent does not influence the course of the decomposition reaction of lead tetraphenyl (Fig. 30).

The displacement of lead from lead tetraphenyl at low temperature was carried out using benzene as solvent. With increase in temperature, the different curves approached each other and intersected at 250°. The higher decomposition values obtained in benzene solution may be explained by the fact that lead tetraphenyl is difficultly soluble in the other solvents, whereas it is readily soluble in benzene.

A number of experiments were made in order to throw light on the nature of the decomposition of lead tetraphenyl; 5.154 g. of the substance and 40 cc. of solvent were used in each experiment under an initial hydrogen pressure of 60 atmospheres, and a temperature of 250° was maintained for 24 hours. In order to determine the solvent effect upon the course of the decomposition of lead tetraphenyl, the experiments were made in both absolute alcohol and ligroin solution.

(1) *Solvent: Absolute Alcohol.*—After the reaction, the alcohol was evaporated leaving as residue a high boiling liquid which crystallized on cooling. Two recrystallizations of this material from alcohol gave a slightly impure product which melted at 66–69°. There is little difference between this melting point and that of *diphenyl.* It is regretted that the product was obtained in such a small amount that the usual organic analysis could not be made. The benzene dissolved in the alcohol was separated by water and converted into *nitrobenzene* by nitration. The nitrobenzene was distilled, yielding 1 g. of the substance. Altogether 2.1 g. of benzene was separated from the alcohol which was about 67% of the theoretical yield. Almost 100% of the lead was displaced from the lead tetraphenyl.

(2) *Solvent: Ligroin.*—For use in these experiments, commercial ligroin was freed from aromatic compounds by treatment with nitrating mixture. It was then distilled on a water bath, the distillate treated again with nitrating mixture, and finally redistilled. The portion distilling between 60 and 80° was used as solvent for the lead tetraphenyl.

The conditions of the experiment using purified ligroin as a solvent were the same as those for the experiments in which absolute alcohol was used. The ligroin obtained at the end of the first experiment contained benzene and was used as solvent for the second experiment. This ligroin on treatment with nitrating mixture yielded 3–4 g. of nitrobenzene. In the first experiment 83% of the lead separated; in the second, 90%. A small amount of diphenyl was present in the residue after the ligroin and benzene were evaporated. Thus, the chief action of hydrogen upon lead tetraphenyl is the displacement of the metal and the hydrogenation of the phenyl radical to benzene; also a direct but insignificant decomposition of lead tetraphenyl into lead and diphenyl:

$$Pb(C_6H_5)_4 \rightarrow Pb + 2C_6H_5—C_6H_5$$

Very interesting results were obtained by heating lead tetraphenyl and lead tetramethyl with water. The first compound remained unchanged, but the second underwent hydrolytic decomposition with the formation of a white crystalline precipitate, the percentage decomposition being about 70%. This decomposition occurred not because of the presence of hydrogen but on account of the low stability of the compound formed under these conditions.

HYDROGENATION OF PHENYL DERIVATIVES OF ELEMENTS OF THE FIFTH GROUP [1]

In the preceding investigation of metallo-organic compounds, it was shown that they are decomposed by the action of hydrogen under pressure with separation of the metal and hydrogenation of the alkyl or aryl radical to the corresponding hydrocarbon. Therefore, it appeared interesting to displace various elements from their compounds having the same radical, e.g., phenyl, and to determine the difference in the stability of the linkages between this radical and the different elements.

For these determinations, equi-molecular solutions of the triphenyl compounds of phosphorus, arsenic, antimony, and bismuth in xylene were used. These compounds were subjected to the action of an initial hydrogen pressure of 60 atmospheres for 24 hours and at the end of the reaction the amount of the elements separated was determined. The general reaction proceeds according to the equation:

$$2(C_6H_5)_3Met + 3H_2 \rightarrow 6C_6H_6 + 2Met$$

A pyrogenetic decomposition with separation of the metal is also possible.

$$2(C_6H_5)_2Met \rightarrow 3C_6H_5—C_6H_5 + 2Met$$

Such decomposition occurred to a greater or lesser extent with each of the above elements, but with arsenic triphenyl it took place almost to the exclusion of hydrogenation whether the reaction was carried out under a pressure of hydrogen or of nitrogen.

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[1] Ipatieff and Razuvaev, Ber., *63*, 1110 (1930).

The separation of phosphorus [1] began at 350°, the same temperature at which phosphorus triphenyl begins to decompose. The latter reaction, however, was not investigated. Under the same conditions no separation of phosphorus took place in the presence of nitrogen.

The displacement of *antimony* occurred at a lower temperature; its pyrogenetic decomposition was also observed, but this proceeded only to a very limited extent. *Bismuth* separated at a still lower temperature and its pyrogenetic decomposition was also slight.

Influence of Time and Pressure.—Antimony triphenyl was used for the study of these factors as it was the most convenient material. The part which these factors play was found to be similar to that observed in the decomposition of lead tetraphenyl; that is, increase in pressure increased the amount of metal displaced. As soon as the pressure reached a certain magnitude, a further increase in pressure did not influence the amount of decomposition. However, duration of heating had a marked influence and it may be stated that the amount of metal separated was almost directly proportional to the time element involved.

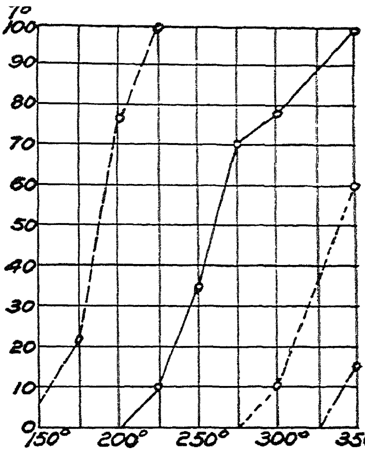

FIG. 31

The results of the experiments are presented in curves (Fig. 31) which express the relationship between the temperature and the amount of metal separated. The duration of each experiment was 24 hours.

From these data it is seen that the stability of the linkages between the phenyl radicals and the elements investigated declines sharply with increase in the metallic properties of the elements in the following order: phosphorus, arsenic, antimony, bismuth.

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[1] Ipatieff, Sr., and Ipatieff, Jr. (Leningrad, 1930) experimented on the displacement of phosphorus from phosphorus trichloride under 100 atmospheres initial hydrogen pressure at 150–160°. The phosphorus trichloride introduced into the high pressure apparatus was contained in a glass tube fitted with a capillary at the top. At the end of the experiment it was found that a considerable quantity of red phosphorus was formed under these conditions in spite of the low temperature. Thus, the white phosphorus which separated was converted into red phosphorus. Under the same conditions, but in the presence of nitrogen, separation of phosphorus does not occur.

Regarding antimony and bismuth, the results obtained are in accordance with data of Michaelis [1] who studied the stability of the linkage of these elements with the phenyl radical. Michaelis came to similar conclusions, based upon his observations regarding the action of concentrated hydrochloric acid upon antimony and bismuth triphenyl.

Hydrogenation of Bismuth Triphenyl.—One one-hundredth mole (4.40 g.) of bismuth triphenyl, $(C_6H_5)_3Bi$, dissolved in 40 cc. of xylene, was poured into a covered glass tube which was placed in the high pressure apparatus to which 10 cc. of xylene had been previously added. To prevent the evaporation of xylene from the glass tube, 60 atmospheres of hydrogen was pumped into the apparatus and the experiment was continued for 24 hours. The separated metal was filtered off, washed, and weighed. Well-formed crystals of the displaced bismuth were observed under the microscope. In these experiments, the metal remaining in solution was determined as follows: The solution, from which the bismuth had been filtered, was combined with the xylene used for washing the metallic bismuth and the walls of the glass tube, and the mixture was subjected to rehydrogenation in the high pressure apparatus, the initial pressure of hydrogen being 60 atmospheres and the temperature 250°. At this temperature, the reaction was quantitative, and the bismuth melted together to form a button at the bottom of the tube. The results are summarized in the following table:

TABLE 85

T., °C.	Bismuth			
	Separated		In Solution, G.	Total Amount, G.
	G.	%		
150	0.144	6.9	1.95	2.094
175	0.460	22.0	1.627	2.087
200	1.593	76.2	0.495	2.088
225	2.078	99.4	0.0	2.078

The pyrogenetic decomposition was studied under conditions similar to those for hydrogenation, i.e., in the presence of 60 atmospheres initial nitrogen pressure for a period of 24 hours. At 200°, an insignificant amount of a white amorphous precipitate separated. The solution of xylene which was filtered off was heated for 24 hours under hydrogen pressure at 225° whereupon about 90% of the bismuth separated as metal.

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[1] Michaelis, Ber., *20*, 54 (1887).

Hydrogenation of Antimony Triphenyl.—This experiment was made under the same conditions as those for bismuth, with 0.01 mole (3.51 g.) of antimony triphenyl, $(C_6H_5)_3Sb$, dissolved in 40 cc. of xylene. The antimony separated in nicely formed crystals. The influence of time of heating was studied under an initial pressure of 60 atmospheres at 275°.

The amount of antimony remaining in solution was about the same as that of bismuth and it was determined by precipitation with hydrogen at 350°, the reaction proceeding quantitatively.

TABLE 86

Hours	Antimony			
	Separated		In Solution, G.	Total Amount, G.
	G.	%		
12	0.522	43.6	0.703	1.225
24	0.849	70.8	0.359	1.208
36	0.445	82.9	0.218	1.213
48	1.210	100.0	0.0	1.210

Effect of Pressure.—This factor was investigated at 275°, the time of heating being 24 hours. The relation between the amount of antimony displaced and the temperature was studied under a hydrogen pressure of 60 atmospheres for an experimental period of 24 hours.

TABLE 87

T., ° C.	Press., Atms.	Antimony			
		Displaced		Separated	
		G.	%	G.	%
225	20	0.544	45.3	0.120	10.0
250	40	0.789	65.8	0.417	34.8
275	60	0.849	70.8	0.897	70.8
300				0.940	78.3
350				1.209	99.3

In order to elucidate the mechanism of the reaction, experiments were made on the displacement of antimony from a solution of antimony triphenyl in ligroin which had been purified so that it did not contain any aromatic hydrocarbons. At the end of the experiment the ligroin was filtered from the separated antimony and treated with nitrating mixture, the resulting nitrobenzene being removed by distillation. A weighed amount (4.793 g.) of antimony triphenyl dissolved in 50 cc. of ligroin was heated for 24 hours, the temperature being gradually increased from 250 to 350°. From this reaction mixture 1.60 g. of antimony separated (amount calculated, 1.64 g.) and a fraction of nitrobenzene was obtained which boiled at 208–210°.

In order to arrive at an understanding of the course of the reaction in the pyrogenetic decomposition of antimony triphenyl, experiments were carried out at 250 and 275° under an initial pressure of 60 atmospheres of nitrogen for a period of 24 hours. After this period at 250°, traces of antimony had separated, while the experiment at 275° gave 0.512 g. of transparent white crystals (insoluble in organic solvents) containing 0.418 g. of antimony—a result corresponding to a 35% separation of antimony. It is possible that this substance is a crystalline oxide of antimony whose formation is due to the oxidation of antimony by oxygen contained in the nitrogen.

Hydrogenation of Arsenic Triphenyl.—As in the preceding experiment, a solution of 0.01 mole of arsenic triphenyl, $(C_6H_5)_3As$, in 40 cc. of xylene was used. As the arsenic was displaced, part of it precipitated on the walls of the glass tube in the form of a mirror. Analysis was made as follows: The precipitated arsenic was filtered off, washed, weighed, and the arsenic mirror was dissolved in a mixture of strong sulphuric and nitric acids and then titrated with iodine according to the method of Robertson.[1] The length of the experiments was 24 hours, the pressure 60 atmospheres.

TABLE 88

T., °C.	Pressure		Antimony
	H_2	N_2	Displaced, %
300	60		10.4
300		60	6.4
350	60		60.7
350		60	66.1

Hydrogenation of Phosphorus Triphenyl.—The displacement of phosphorus began at a relatively high temperature, 350°, under hydrogen pressure only. The phosphorus separated as solid drops of white phosphorus colored red by admixture with much red phosphorus. The gas at the end of the reaction contained a small amount of phosphine. At a higher temperature the compound decomposed to a greater extent. Thus, it was necessary to limit experiments to a temperature not exceeding 350°. The conditions were as previously stated, namely, 0.01 molar solution and initial hydrogen pressure of 60 atmospheres. At the end of the experiment, the gas was passed through a solution of silver nitrate to determine the amount of phosphine (from which the phosphoric acid was precipitated by ammonium molybdate solution). On the bottom of the glass tube, phosphorus was present in the form of red solid drops, and the amount was determined by oxidation with nitric acid and precipitation by ammonium molybdate solution.

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[1] Robertson, J. Am. Chem. Soc., *43*, 182 (1921).

Experiment No. 1.—After oxidation of the separated phosphorus, 3.2385 g. of ammonium phosphomolybdate was obtained, i.e., 17.3% of the phosphorus had separated. The gas gave 0.0961 g. of ammonium phosphomolybdate, corresponding to 0.005% of the phosphorus.

Experiment No. 2.—After oxidation of the separated phosphorus, 2.9100 g. of ammonium phosphomolybdate was obtained, corresponding to 15.5% of the phosphorus. When nitrogen was substituted for hydrogen, under the conditions indicated, no separation of phosphorus occurred.

CONCLUSIONS

(1) Hydrogenation of metallo-organic compounds under pressure causes displacement of the metal and the corresponding hydrocarbon is formed.

(2) Under certain conditions of temperature, pressure, and time, certain elements can be displaced quantitatively from metallo-organic compounds by hydrogen. Therefore, this reaction may be recommended for the quantitative determination of the elements present in such metallo-organic compounds.

HYDROGENATION AND DECOMPOSITION OF SILICON COMPOUNDS [1]

The preceding investigations involving the hydrogenation of tetraphenylmethane showed that tetracyclohexylmethane cannot be obtained readily by hydrogenation under pressure in the presence of a nickel oxide catalyst. However, it was of interest to investigate the possibility of hydrogenating silicon tetraphenyl, $(C_6H_5)_4Si$, so as to obtain a completely hydrogenated product.

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[1] Ipatieff and Dolgov, Ber., *67*, 1220 (1929).

Today, as a result of experiments conducted by various scientific workers, it is possible to obtain various organic silicon compounds. In spite of a complete analogy and similarity between many compounds of carbon and of silicon a great difference exists between these compounds which may be explained by the different character of the silicon and carbon atoms. The carbon atom is amphoteric and, therefore, able to combine with various positive and negative elements as well as with other carbon atoms forming a great variety of aliphatic and cyclic compounds. The preference of silicon is for negative rather than positive linkages since the silicon atom possesses a clearly defined positive character. On account of this characteristic its hydrides, with the exception of silicane (SiH_4), are less stable and may be readily oxidized by alkali and water. With oxygen a stable linkage is formed resulting in the formation of cyclic and non-cyclic compounds, siloxane and siloxene. The tendency of organic silicon compounds towards polymerization is more strongly manifested than in the case of true organic compounds.

The old viewpoint of Woehler, as well as the opinion of Ladenburg,[1] must be revised regarding the complete analogy of silicon and carbon compounds, especially since it has been shown by Moissan and Stock that no such similarity exists between carbon and silicon.

Thus, it seemed interesting to investigate the stability of the linkage of silicon and carbon in high molecular organic silicon compounds, and to compare it with the derivatives of tri- and tetraphenylmethane which had been previously studied.

It is known that in silicon carbide the linkage between carbon and silicon is very stable. The lower members of the mono-alkyl silicane series were obtained by Stock [2] but these substances are not very stable. Stock also obtained methyl-, dimethyl-, and triethyl silicane [SiH_3CH_3, $SiH_2(CH_3)_2$, and $SiH(C_2H_5)_3$]. The tetrasubstituted compounds are quite stable, their stability increasing with increase in weight of the hydrocarbon radicals attached to the central silicon atom. Carbon compounds show

[1] Ladenburg, Ber., *5*, 588 (1872).

[2] Stock, Z. Electrokhem., *32*, 345 (1926).

opposite tendencies. Tetraphenylsilicane, $(C_6H_5)_4Si$, may be obtained quite easily, while tetraphenylmethane is obtained with considerable difficulty and only in small yield. In all cases where its formation is anticipated, triphenylmethane is formed. Tetrabenzylmethane is unknown at the present, but tetrabenzylsilicane may be obtained in satisfactory yield according to Polis.[1] It distills without decomposition at 550°. Hexaphenylethane is unstable and decomposes into triphenylmethyl.[2] Hexaphenyldisilicane was prepared by Schlenk[3] who found that it melts without decomposition at 354°. It does not show the slightest tendency to decompose.

The problem of studying hydrogenation and decomposition of certain ethyl- and phenylsilicanes at high temperature and pressure was considered. The experiments were carried out in a 250-cc. high pressure apparatus. The substance was placed, without solvent, in a glass tube in the high pressure apparatus. The conditions of the experiments varied, e.g., the temperature varied from 300 to 500°; the initial pressure, from 30 to 80 atmospheres; the duration of the experiment, from 1 to 10 days.

Hydrogenation of Tetraethylsilicane.—By heating tetraethylsilicane, $(C_2H_5)_4Si$, for 3 days at 360–500°, there was obtained both a decomposition product and a condensation product according to the equation:

$$2Si(C_2H_5)_4 \rightarrow 2C_2H_6 + (C_2H_5)_3\text{—}Si\text{—}Si\text{—}(C_2H_5)_3$$

In this case, the group $(C_2H_5)_3Si$— has a tendency to combine with itself to form a saturated compound, leading to the formation of *hexaethyldisilicane.* Among the gaseous products, in addition to methane and ethane, there was also a small amount of silicane (SiH_4) as indicated by the appearance of a white smoke during burning of the mixture. Perhaps more condensation occurred than was realized, since a small amount of a dark, thick oil remained in the distilling flask. It is supposed that in this case *triethylsilicane* was formed also, but its presence could not be ascertained with certainty due to the small yield.

Hydrogenation of Triethylphenylsilicane.—After 24 hours of heating at 450°, triethylphenylsilicane, $(C_2H_5)_3(C_6H_5)Si$, gave only 15% of decomposition products, while after 3 days of heating at 350° the formation of decomposition products totaled 60%. The following substances were isolated: undecomposed *triethylphenylsilicane*, *benzene*, *hexaethyldisilicane*, *triethylsilicol*, *tetraethylsilicane*, and *diethyldiphenylsilicane*. The general scheme of the decomposition may be presented as follows:

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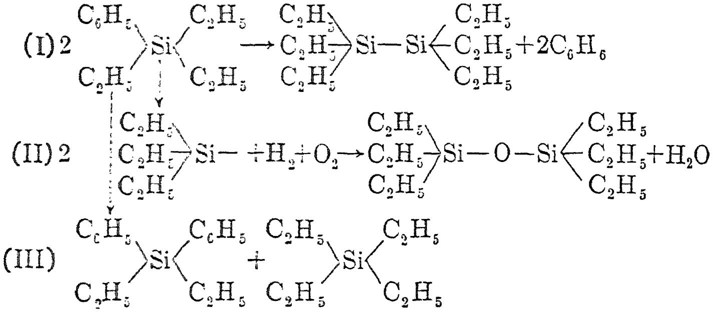
[1] Polis, Ber., *19*, 1023 (1886).

[2] Gomberg, Ber., *30*, 2043 (1897).

[3] Schlenk, Ber., *44*, 1178 (1911).



The origin of hexaethyldisilicane, according to scheme I, is explained quite satisfactorily by its formation from tetraethylsilicane, scheme III. The presence of an oil containing oxygen (to which was ascribed the structure of hexaethylsiloxone) was due to the reaction indicated in scheme II. Its formation may be explained by the action of the oxygen of the air present in the apparatus at the beginning of the experiment. The amount of the last product was insignificant since the amount of oxygen present was small. From scheme III it is seen that phenyl and ethyl groups may interchange places, depending upon the experimental conditions, forming diethyldiphenylsilicane and tetraethylsilicane.

Hydrogenation of Tetraphenylsilicane.—Tetraphenylsilicane, $(C_6H_5)_4Si$, proved to be a very stable compound in spite of the fact that in a whole series of experiments the temperature was varied between 300 and 450°. After 1 hour of heating at 450° it merely sublimed, forming needles about 1 cm. long. At the end of the reaction, the entire mass was almost unchanged but it contained 2 g. of a yellowish oil which was not investigated thoroughly. It is interesting to compare the stability of tetraphenylsilicane with that of tetraphenylmethane; in the latter the phenyl radical is split off at 250–260° under pressure and the result is triphenylmethane.

At 490° a complete decomposition of the tetraphenylsilicane molecule occurred, accompanied by extensive condensation. The crystalline substance obtained did not melt, or dissolve in any solvent, nor could it be distilled or sublimed. The mass of crystals discernible under the microscope was insoluble both in acids and alkalies; drops of oil were also visible. On ignition, the crystals puffed up and were converted into a lustrous black substance.

Tetraethylsilicane was prepared according to the method of Polis [1] from silicon tetrachloride and ethyl bromide by the action of sodium in dry ether solution. After washing with sulphuric acid and several distillations, a product was finally obtained which melted at 153–155°, d_{15}^{15}, 0.7763.

The decomposition of tetraethylsilicane under various pressures of hydrogen was studied at several temperatures and contact times. In each experiment 25 g. of the substance was placed in a glass liner in the high pressure apparatus. The percentage decomposition of the substance at a given temperature depended on the duration of heating and the pressure. *Ethane* and *silicane* (SiH_4) were found in the gas after the reaction, the amount of ethane increasing with increase in temperature.

The liquid product of the decomposition reaction was a colorless, mobile liquid of characteristic odor. The first distillation gave the following fractions: (1) 150–158° (40–80%); (2) 160–170° (1–4%); (3) 224–225° (5–30%); (4) over 250° (10%).

The first fraction (b.p., 150–158°) contained undecomposed *tetraethylsilicane.* After washing with sulphuric acid and distillation over sodium it boiled at 153–157°.

Anal. Calcd. for $C_8H_{20}Si$: C, 66.7; H, 13.9; mol. wt., 144. Found: C, 66.5; H, 14.0; mol. wt., 143 (in benzene).

Fraction No. 3 (b.p., 224–225°) contained *hexaethyldisilicane.*

Anal. Calcd. for $C_{12}H_{30}Si_2$: C, 62.6; H, 13.0; mol. wt., 230. Found: C, 62.6; H, 13.3; mol. wt., 228 (in benzene).

After distillation, a thick dark oil remained in the flask which boiled above 250°, doubtless condensation products.

Triethylphenylsilicane was obtained by the method of Bygden [2] from phenyltrichlorsilicane and ethylmagnesium bromide in ether solution. Phenyltrichlorsilicane was obtained according to the method of Bygden and Kipping.[3] The triethylphenylsilicane boiled at 237–247°; d_{15}^{15}, 0.906. This derivative of silicon decomposed more readily than tetraethylsilicane. It underwent 60% decomposition yielding a series of decomposition products when heated 4 hours at 300–320° under an initial hydrogen pressure of 80 atmospheres.

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[1] Polis, Ber., *19*, 1203 (1886).

[2] Bygden, Ber., *45*, 709 (1912).

[3] Bygden and Kipping, J. Am. Chem. Soc., *91*, 214 ff. (1907).

The gaseous products contained about 4% of saturated hydrocarbons and traces of silicane. The liquid product of the reaction was a yellow oil with a green fluorescence. Distillation gave the following fractions: (1) up to 180° (760 mm.); (2) 195–216° (760 mm.); (3) 140–141° (50 mm.); (4) 170–184° (50 mm.); (5) above 200°.

The first fraction (up to 180°) generated hydrogen energetically when warmed with sodium, which indicated the presence of a compound containing oxygen. In order to isolate this compound, the 180° fraction was treated with sodium hydroxide solution; the lower alkaline layer was separated, acidified with hydrochloric acid, and the oil rising to the top was dried with sodium sulphate and distilled. About 0.5 g. of a substance boiling at 152–157° was obtained. Due to insufficient quantity, it was impossible to make a complete study of this compound, but according to its molecular weight and odor it may be considered to be either *triethylsilicol*, or a related compound.

Anal. Calcd. for $C_6H_{16}OSi$: C, 54.5; H, 12.1; mol. wt., 132. Found: C, 55.5; H, 11.7; mol. wt., 140 (in benzene).

In all probability this substance owed its formation to the presence of oxygen (from the air) in the apparatus before the hydrogen was pumped in. In experiments where air was displaced from the apparatus by hydrogen this compound was not obtained. Calculations show that the amount of oxygen present in the bomb of 50 cc. capacity is sufficient for the formation of 0.54 g. of silicol.

After the silicol was separated, the first fraction was distilled. The fraction boiling at 79–82° was identified as benzene. Reaction with nitrating mixture produced nitrobenzene and from the latter aniline was derived which gave a violent coloration with calcium hypochlorite. In addition to benzene, benzene sulphonic acid was also obtained.

The remaining oil was washed with sulphuric acid and distilled over sodium. From the fraction boiling at 135–158°, *tetraethylsilicane* (b.p., 147–153°) was isolated.

Anal. Calcd. for $C_8H_{20}Si$: C, 66.7; H, 13.9; mol. wt., 144. Found: C, 66.5; H, 14.0; mol. wt., 142 (in benzene).

The formation of tetraethylsilicane from triethylphenylsilicane shows the tendency of an asymmetrically substituted silicane to rearrange itself into a compound of symmetrical structure.

The second fraction (195–216°) contained unchanged triethylphenylsilicane; d^{15}_{15}, 0.8889; (Bygden) d^{15}_{4}, 0.894.

Anal. Calcd. for $C_{12}H_{20}Si$: C, 75.0; H, 10.4; mol. wt., 192. Found: C, 74.6; H, 10.6; mol. wt., 194 (in benzene).

This fraction was not homogeneous. With nitrating mixture, a dark crimson coloration was imparted to the substance which disappeared on dilution with water. Hydrochloric acid gave an intense red coloration. The oil dissolved in strong sulphuric acid and when heated, assumed a pale yellow color.

Both fractions were distilled under diminished pressure (50 mm.) and the following fractions were obtained: (1) 138–144°; (2) 148–190° (a few drops); (3) 210–220°; (4) 222–240°; (5) residue above 250°.

The first fraction (b.p., 138–144°, 50 mm.) consisted chiefly of triethylphenylsilicane as shown by the analytical data. Only the third fraction (210–220°), which was very small, corresponded to *hexaethyldisilicane.*

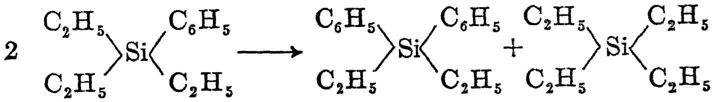
Anal. Calcd. for $C_{12}H_{30}Si_2$: C, 62.6; H, 13.0; mol. wt., 230. Found: C, 61.9; H, 13.4; mol wt., 228 (in benzene).

This hexaethyldisilicane may have originated in either of two ways: (1) from triethylphenylsilicane by the splitting of the phenyl group and the combining of the two triethylsilicyl groups; or (2) from two molecules of tetraethylsilicane by an analogous condensation with the splitting of one ethyl group from each molecule.

The fourth fraction (22–240°, 5 mm.) distilled at 300–312° under ordinary pressure.

Anal. Calcd. for $C_{16}H_{20}Si$: C, 75.9; H, 9.3; mol. wt., 216. Found: C, 75.3; H, 9.2; mol. wt., 216 (in benzene).

According to the molecular weight, this compound (a yellow oil with characteristic odor) may be considered as diethyldiphenylsilicane, originating from two molecules of triethylphenylsilicane by an exchange of radicals.



$$2\ \substack{C_2H_5\\C_2H_5}{>}Si{<}\substack{C_6H_5\\C_2H_5} \longrightarrow \substack{C_6H_5\\C_2H_5}{>}Si{<}\substack{C_6H_5\\C_2H_5} + \substack{C_2H_5\\C_2H_5}{>}Si{<}\substack{C_2H_5\\C_2H_5}$$

The fifth fraction boiled at 251–260°. It was straw colored and of the consistency of liquid honey. Determination of its structure was unsuccessful, but according to its molecular weight it may be inferred that it was a *dimer* of the initial triethylphenylsilicane.

Anal. Calcd. for $C_{24}H_{40}Si_2$: mol. wt., 392. Found: 382, 386 (in benzene).

Tetraphenylsilicane was obtained by the method of Polis [1] by the action of sodium on an ether solution of silicon tetrachloride and chlorbenzene. After the excess sodium had been dissolved in alcohol, the powdered precipitate was extracted by benzene and the silicic acid separated by suction filtration. After crystallization, white crystals melting at 228° were obtained. Attempts to obtain tetraphenylsilicane from phenyltrichlorsilicane and phenylmagnesium bromide according to the method of Grignard were unsuccessful. Because of the peculiar stability of the compound, a series of hydrogenation experiments was made at various temperatures.

TABLE 89

Expt. No.	T., °C.	Initial Press., Atms.	Duration of Expt., Hrs.	Remarks
1	230	96	144	No reaction
2	350	80	72	" "
3	380	80	53	" "
4	400	60	48	" "
5	450	75	192	" "
6	490	60	96	Condensation reaction

In Expts. 5 and 6 a part of the tetraphenylsilicane sublimed forming beautiful white shining crystals which, after recrystallization from benzene, melted at 234°. They felt oily to the touch and left grease spots on paper. No formation of benzene or diphenyl was observed, nor did any decomposition occur.

In Expt. 6 very little silicane was present in the gas remaining after the reaction. On the gasket of the apparatus a white crystalline sublimate was observed which, after crystallization from benzene, melted at 234°; it was unchanged tetraphenylsilicane.

The product remaining in the tube of the apparatus in the sixth experiment consisted of a crystalline substance with some black incrustations. This substance was treated with ether, whereupon the incrustations assumed a yellowish color. After removal of the ether, drops of an oily liquid remained. The remaining crystals were insoluble in both ether and benzene and, therefore, could not be tetraphenylsilicane. They did not dissolve in boiling xylene and, therefore, were not hexaphenylsilicane. They were also insoluble in naphtha, acetone, alcohol, and toluene and, therefore, they were not triethylphenylsilicane or naphthalene. When these crystals were introduced into a flame, they melted and were converted into black spheres. They sublimed but did not distill. The oily drops were invisible under the microscope, and the substance presented a clearly defined crystalline structure, the crystals having black incrustations. These black incrustations were insoluble in acids and in alkalies, and therefore, were not amorphous silicon. Perhaps under the influence of pressure and high temperature a deep seated condensation occurred with the formation of a very complex compound. An attempt to investigate this substance more thoroughly was unsuccessful.

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[1] Polis, Ber., *18*, 1540 (1885).

In order to decompose this condensation product, 5 g. of it was heated with benzene at 450–490° for 3 hours. After cooling, it was evident that no reaction had taken place, and the benzene did not extract any material.

This investigation of the hydrogenation of organic silicon compounds was the first attempt in this direction. Dolgov[1] continued these experiments with organic silicon compounds containing oxygen in order to study the stability of the various linkages of silicon with carbon, oxygen, silicon (Si—C and Si—O, Si—Si), etc.

CONCLUSIONS

(1) Tetraethylsilicane splits off *ethane* under the influence of hydrogen pressure at 350–360° and is converted into hexaethyldisilicane.

(2) Under similar conditions triethylphenylsilicane splits off benzene and forms *hexaethyldisilicane.* In addition, there is an interchange of radicals of triethylphenylsilicane which results in the formation of *diethyldiphenylsilicane* and *tetraethylsilicane.*

(3) *Tetraphenylsilicane* does not undergo any change within the temperature range of 260–456°, but at 490° a marked condensation takes place whereby it is converted into a compound

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[1] Dolgov and Volnov, Russ. Phys. Chem. Soc. (1930) (1933).

of unknown structure which neither distills, melts, sublimes, or dissolves in any of the usual solvents.

(4) The asymmetrical derivatives of silicane have a tendency to change into symmetrical derivatives under the experimental conditions indicated above.

(5) Experiments on the hydrogenation of tetraphenylsilicane showed that in spite of the use of high temperatures, it is impossible to obtain *tetracyclohexylsilicane*. The stability of the linkage of the central atom of silicon with the phenyl groups is of particular interest.

(6) The stability of silicon compounds containing aromatic radicals leads to the question whether silicon compounds similar to those indicated above do not participate in the formation of aromatic brown coal tar. Calculations on the normal ash of coals which have a high content of silica indicate that the silicon might be present in combination with a considerable part of the organic substances of the coal. It is to be inferred that vegetation, from which brown coal originates, also contained silicon in the form of complex organic silicon compounds. In the process of coking at high temperature, conditions similar to those of the above experiments are encountered which may result in the decomposition of the organic silicon compounds with separation of aromatic substances. Thus, it is safe to assume that at least a part of the benzene formed by coking brown coal at high temperature comes from the organic silicon compounds.

CHAPTER VIII

DESTRUCTIVE HYDROGENATION OF ORGANIC COMPOUNDS [1]

Almost from the beginning of my investigations in 1904 on the pyrolysis of organic compounds under pressure it was noted that the regular increase in pressure with increase in temperature was broken whenever the process was accompanied by decomposition of the initial substance; the value of the coefficient (dp/dt) increased and the pressure curve offered the possibility of determining the degree of dissociation at the temperatures in question. Desiring to accelerate the course of the reaction which was slowed down by decrease in pressure, it was decided to work in the presence of various catalysts. The iron walls of the bomb itself were found to be active catalysts for dissociation. The dissociations studied at this time were accompanied by the separation of hydrogen.

At this time, 1905–1906, it was also decided to conduct these decompositions under pressure not only of the vapors of the substance itself, but also of *hydrogen introduced from the outside.* This investigation showed that the course of pyrolysis depended a great deal upon the presence or absence of hydrogen pressure. In the presence of hydrogen the products were more highly hydrogenated than in its absence although no active catalyst such as nickel was added, the reaction being made in a steel bomb.

Several years after these investigations (1913), a German engineer, Bergius, was issued two patents. The first patent protected the method for obtaining light hydrocarbons from heavy hydrocarbons under the action of heat and was distinguished by the fact that hydrocarbons were hydrogenated under conditions of pressure and temperature by means of hydrogen which was pumped in before the experiment. In the second patent, Bergius obtained protection on methods for treating brown coal and analogous substances, obtained by natural or artificial carbonization, by hydrogen. The treatment with hydrogen under high pressure is continued until there is no longer any conversion of the brown coal into liquid products. Furthermore, this hydrogenation according to Bergius' method can be applied only to brown coals which do not contain too high a percentage of carbon.

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[1] Ipatieff, "Hydrogenation under Pressure," a paper given at Symposium of the Eighth Congress of Industrial Chemistry in Strasbourg, France, June 26, 1928.

The French engineer Kling, who studied the details of the Bergius method for liquefying coal, as well as for the pyrolysis of heavy hydrocarbons, was also familiar with the research published by the author of this book from 1904 to 1913 and he writes in Chimie et Industrie:[1] "The analogy between the method of Ipatieff and the method that was the subject of the patent of Bergius is indisputable." Travers[2] reached the same conclusion and considered that Bergius merely applied the method of Ipatieff, namely, hydrogenation under pressure. Kling, in the above-mentioned article, writes that Ipatieff had the idea of carrying out the pyrolysis of organic compounds not only under the pressure determined by the volatility of these substances, but also in the presence of hydrogen introduced at the beginning of the experiment, the average initial pressure being 100 atmospheres.

These investigations of Ipatieff showed that pyrolysis proceeds in two entirely different ways, depending on whether it is conducted in the absence or in the presence of hydrogen introduced under pressure at the beginning of the experiment. They also showed that in the latter case the products were more hydrogenated than in the first case and also that the metal from which the autoclave was constructed played a significant part in the process.

The previous investigations of the writer on the hydrogenation of various organic compounds under pressure in the absence of added active catalysts have shown that the results depend on the iron walls of the autoclave for catalytic effects. The true effect of the last-mentioned factor was established by a series of experiments.

It should be noted that the works of Berthelot concerning the action of hydrogen iodide on organic compounds showed the possibility of hydrogenation by means of the hydrogen *in statu nascendi*. Moreover, the famous organic chemist, Emil Fischer, delivered a speech in 1912 with reference to a problem of the

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[1] Kling, Chimie & industrie, *9*, 389–399 (1923); C.A., *17*, 2038 (1923).

[2] Travers, Chimie & industrie, *13*, 373–382, 722–730 (1925); C.A., *19*, 2303 (1925).

"Institute for the Study of Coal" in which he pointed out that "it would be very desirable to carry out experiments on coking in an atmosphere of hydrogen whereby, in all probability, it would be possible to increase the yield of ammonia and also of volatile carbon compounds, particularly hydrocarbons." He stated further that "the question of the influence of pressure upon coking should be studied more thoroughly." He also said "how wonderful it would be to obtain chiefly liquid fuels from their respective solids by means of a suitable reduction process." It appeared to him that the principal problem of the coal industry was the solution of this problem and for this purpose all available present-day technique and science should be employed. Furthermore, Fischer pointed out that high yields of liquid hydrocarbons from brown coal might be expected, especially in the presence of a catalyst.

In addition to these historical references, there might also be mentioned the work undertaken by Bergius who introduced a new idea in the utilization of solid fuel and gave impetus to technical and scientific thought toward working out better methods of improving the quality [1] of various kinds of fuels and making possible their more economical utilization. In many countries intensive work has been done on the pyrolysis of various substances under pressure in order to obtain a high grade gasoline. The petroleum industry has adopted certain changes in the cracking process, e.g., cracking under pressure and in the presence of hydrogen.

Destructive Hydrogenation of Naphthalene.[2]—The first theoretical work regarding the hydrogenation of organic compounds at temperatures close to their temperatures of decomposition was carried out by us on naphthalene. Previous work on the hydrogenation of naphthalene under pressure at a temperature below 300° showed that the first product was *tetrahydronaphthalene,* almost in theoretical yield, and that further hydrogenation of this compound under pressure led to the formation of decalin. The phenomenon of the joint action of catalysts (promoter action) permits a considerable decrease in the temperature of hydrogenation, especially with organic substances containing oxygen, such as camphor, fenchone, etc. Alumina was found to be an excellent promoter for nickel oxide and the nickel oxide-alumina combination, which I first introduced for ordinary hydrogenation, was also applied in the study of the decomposition of organic compounds in the presence of hydrogen under pressure.

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[1] It is necessary to note, however, that experiments carried out on an industrial scale involving berginization of solid fuels did not lead to the desired results. It was found to be uneconomical to subject only the solid fuel to pyrolysis and, therefore, the method of Bergius had to be revised; the I.G.A. worked out a new method for ennobling various kinds of fuel.

[2] Ipatieff and Klukvin, "Pyrolysis of Naphthalene," News of the Scientific Technical Department of V.S.N.H., 1923, Ber., *58*, 1 (1925).

From the first experiments with naphthalene it was evident that if the temperature of hydrogenation was increased to 400°, a decomposition of the products of hydrogenation took place and a series of aromatic hydrocarbons was obtained. A small amount of gas was formed and the residual gas was chiefly hydrogen. The product of the reaction contained more than 30% of aromatic hydrocarbons and 20% of naphthalene which had not reacted, the remainder being tetrahydronaphthalene. The reaction evidently proceeded in such a way that the decomposition of tetrahydronaphthalene occurred at the moment of its formation and its hydrogenated ring split in various directions with the formation of mono- and disubstituted benzenes.

For each of these experiments, 40–60 g. of naphthalene and 3 g. of catalyst (50% NiO and 50% Al_2O_3) were placed in the high pressure apparatus and hydrogen pumped in to 100 atmospheres pressure. The reaction was continued for 25 hours at 450–480°, the average drop in pressure being 40 atmospheres. In many of the experiments analysis was made of the residual gas. (See following table.)

TABLE 90

EXPT. NO.	CO_2	C_nH_{2n}	O_2	CO	H_2	CH_4	N_2
1	1.6	0.0	0.8		88.8	3.2	5.8
2	1.2	0.0	0.4		90.0	4.8	3.6
3	0.8	0.0	0.8		91.6	1.2	5.6
4	0.8	0.0	0.8		87.6	4.4	7.9
5			0.8	0.4	91.2	1.8	6.1

According to the above data, the gas consisted chiefly of *hydrogen* with a small content of methane; unsaturated hydrocarbons were entirely lacking. The liquid reaction product was brownish in color with a tendency towards opalescence; naphthalene separated on standing.

One thousand grams of product was subjected to fractional distillation. The resulting data are summarized in the following table.

TABLE 91

Fraction No.	Boiling Point, ° C.	Specific Gravity at 20° C.	n_D^{15}	Weight, G.
1	45– 80	0.8214	1.4643	15
2	80– 85	0.8551	1.4846	15
3	85–105	0.8580	1.4870	15
4	105–115	0.8579	1.4881	30
5	115–130	0.8613	1.4900	45
6	130–140	0.8678	1.4942	37
7	140–145	0.8641	1.4958	
8	145–150	0.8763	1.4967	27
9	150–155	0.8873	1.4991	
10	155–160	0.8878	1.5010	
11	160–165	0.8998	1.5026	11
12	165–170	0.9001	1.5051	
13	170–180	0.9091	1.5100	
14	180–191	0.9488	1.5232	34
15	191–195	0.9617	1.5330	118
16	195–199	0.9848	1.5380	42
17	199–201	0.9848	1.5100	247
18	201–203	0.9899	1.5400	101
19	203–205	0.9890	1.5470	136

The fractions were readily sulphonated and nitrated. The fraction boiling at 80–85° gave on nitration *nitrobenzene* (b.p., 208°) and *dinitrobenzene* (m.p., 87°); which made it evident that the original material was benzene.

The fraction boiling at 105–115° was refractionated. The product boiling at 109–112°, on treatment with nitric acid, formed a nitro compound boiling at 218–240° which by repeated nitration gave trinitrotoluene (m.p., 79°). According to the method of Kaminsky, oxidation of this fraction with chromic acid mixture in the presence of hydrogen chloride at ordinary pressure gave *benzoic acid*. In view of these data, this fraction consisted chiefly of *toluene*.

By repeated distillation of the fractions boiling at 130–140° and 140–145°, a fraction boiling at 140–142° was separated which gave only liquid products on nitration. By oxidation of these fractions with chromic and hydrochloric acids, orthophthalic acid was obtained and therefore it was to be assumed that *o-xylene* was originally present.

The analysis and other properties of the fraction boiling at 170 to 180° showed it to consist mainly of benzene hydrocarbons.

Anal. Calcd. for $C_{10}H_{14}$: C, 89.5; H, 10.5. Calcd. for $C_{10}H_{12}$: C, 90.9; H, 9.1. Found: C, 90.0; H, 10.0.

The fractions boiling at 180–191° and 191–195° were redistilled and separated into two fractions, boiling at 178–186° and 186–199°, respectively. The following analyses indicate that these fractions consisted chiefly of *benzene hydrocarbons.*

TABLE 92

Fraction No.	Boiling Point, °C.	Analysis, Found	
		% C	% H
1	178–186	90.0	9.9
2	186–199	90.2	9.7

By repeated distillation of fractions 16–18, a fraction boiling at 196 to 201° was separated, naphthalene remaining in the distilling flask.

Anal. Calcd. for $C_{10}H_{12}$: C, 90.9; H, 9.1. Found: C, 90.3; H, 9.1.

This fraction boiling at 196–201° contained a considerable amount of tetrahydronaphthalene.

Fraction 19 which boiled at 203–205° and had a specific gravity of 0.9865 was pure tetrahydronaphthalene.

Anal. Found: C, 90.6; H, 8.9.

The fraction boiling at 196–201° was hydrogenated further in the presence of nickel oxide under pressure to pure *decahydronaphthalene:* b.p., 183–187°; d_{15}, 0.8777 and n_{15}, 1.4757.

Anal. Calcd. for $C_{10}H_{18}$: C, 87.0; H, 13.0. Found: C, 86.9; H, 13.1.

When the hydrogenation of tetrahydronaphthalene was conducted under pressure at 400° in the presence of a mixed catalyst (aluminum oxide and nickel oxide is the ratio of 1: 1), decomposition occurred with the formation of benzene hydrocarbons.

HYDROGENATION OF AROMATIC COMPOUNDS NEAR THEIR DECOMPOSITION TEMPERATURES (DESTRUCTIVE HYDROGENATION) IN THE PRESENCE OF VARIOUS CATALYSTS

The high pressure hydrogenation of aromatic compounds near their decomposition temperatures in the presence of mixed catalysts was first carried out by Ipatieff and Klukvin [1] in 1924 with the hope that a systematic study of the decomposition of aromatic compounds during hydrogenation at high temperatures and pressures would help to explain what occurs in cracking in the presence of hydrogen under high pressure.

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[1] Ipatieff and Klukvin, Proceedings of Academy of Sciences of Russia, Leningrad, 1924; Ber., *58*, 1–3 (1925).

From the start, this work immediately showed the possibility of drawing important conclusions which were later confirmed by Ipatieff and Orloff,[1] Orloff,[2] Orloff and Belopolsky,[3] Orloff and Lichatschew,[4] and also by Kling and Florentin.[5] These investigations showed that aromatic compounds can be hydrogenated even at the high temperature of 450°, but that the products of hydrogenation decompose, and, as the temperature increases, further decomposition takes place without the formation of carbon.

The first important question to be answered concerned the hydrogenation of aromatic compounds in the presence of molybdenum oxide.[6] Previously it was not known that monocyclic aromatic compounds could be hydrogenated at high pressure under the influence of catalysts other than those of nickel (Ni, NiO). Therefore, experiments were made first on the high temperature (450°) hydrogenation of benzene and xylene under pressure in the presence of molybdic oxide catalyst (MoO_3).[7] Neither benzene nor xylene hydrogenated in the presence of the molybdenum catalyst, but under these conditions xylene decomposed forming benzene and toluene. In the presence of alumina the demethylation of xylene to benzene and toluene increased with increase in temperature.

A second series of experiments was made for the purpose of hydrogenating naphthalene in the presence of different catalysts such as nickel oxide, cupric oxide, and ferric oxide, even though hydrogenation occurred in their absence since the iron walls of the autoclave acted catalytically.

Preliminary experiments with fluorene showed that hydrogenation takes place at high temperature in the presence of molybdenum catalysts. Therefore, polycyclic aromatic compounds differ from monocyclic compounds under these conditions of hydrogenation.[1]

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[1] Ipatieff and Orloff, Ber., *60*, 1963 (1927).

[2] Orloff, Ber., *60*, 1950 (1927).

[3] Orloff and Belopolsky, Ber., *62*, 1226 (1929).

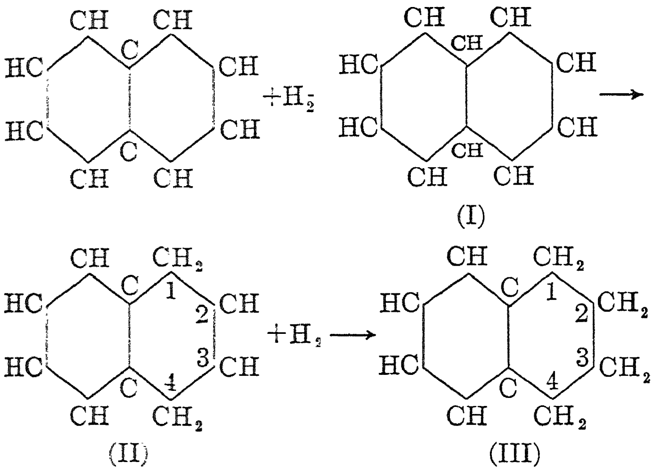
[4] Orloff and Lichatschew, Ber., *62*, 719 (1929).

[5] Kling and Florentin, Compt. rend., *182*, 526 (1926).

[6] The molybdenum oxide catalyst was usually prepared by precipitating C.P. ammonium molybdate with nitric acid; in some cases C.P. molybdenum trioxide (MoO_3) was used.

[7] Ipatieff, J. Am. Chem. Soc., *55*, 3696 (1933).

In the case of naphthalene an explanation can be given as to why hydrogenation occurs under the influence of different catalysts. Naphthalene differs from monocyclic hydrocarbons in that it has two common atoms of carbon. It is assumed that the addition of an atom of hydrogen occurs first at the common atoms of carbon (I); the product is at once isomerized into 1, 4-dihydronaphthalene forming an ordinary double bond in the ring (II), and their further hydrogenation takes place easily giving 1, 2, 3, 4-tetrahydronaphthalene (III).



(I)

(II)

(III)

This assumption is supported by the fact that sodium amalgam hydrogenated naphthalene to 1, 4-dihydronaphthalene (II) which might be transformed into 2, 3-dihydronaphthalene under the influence of sodium ethoxide.

Another point to be decided from consideration of the results of destructive hydrogenation is whether hydrogenation occurs first and is followed by decomposition. Experiments with nickel catalyst indicated that hydrogenation occurred first, and experiments with molybdenum catalysts confirmed this indication.

When the temperature of hydrogenation of naphthalene did not exceed 450° the product was almost entirely tetrahydronaphthalene, but when hydrogenation occurred above 450°, the tetrahydronaphthalene first formed decomposed into benzene hydrocarbons; the presence of hydrogen was necessary to avoid carbon formation. It should be mentioned that in the decomposition of tetrahydronaphthalene into benzene hydrocarbons, naphthenes were found in all fractions only when using nickel catalyst. This fact shows that during decomposition some molecules of the monocyclic aromatic compounds were hydrogenated.[1] Only in the presence of molybdenum catalysts was cyclohexane found in the first fractions of the benzene hydrocarbons; but this hydrocarbon can be assumed to be a decomposition product of tetrahydronaphthalene since at lower temperatures (below 450°) no cyclohexane was formed.

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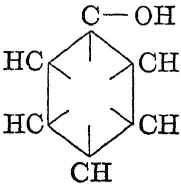
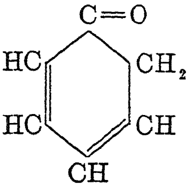
[1] It is hoped that experiments in this direction with other polynuclear hydrocarbons will explain the general cause of this reaction.

Another series of hydrogenations was made with phenol at high temperature in the presence of different catalysts as it was interesting to explain the nature of the hydrocarbons obtained. Investigations of Tropsch,[2] Orloff,[3] and Kling and Florentin [4] concerning the conversion of phenols into hydrocarbons showed that under certain conditions, e.g., at high temperature and pressure (with nickel oxide or molybdenum), hydrogenation of the aromatic ring occurred and cyclohexane was obtained, but its amount depended largely upon the nature of the catalyst used.

The possibility of hydrogenating the aromatic ring under the above-mentioned conditions can be explained in the following manner, as was assumed in 1905 [5] when for the first time phenol was hydrogenated under pressure in the presence of nickel oxide. The products of hydrogenation were cyclohexanol and cyclohexanone, the amount of the latter being greater at a low temperature of hydrogenation. This reaction was explained by the fact that phenol has two tautomeric forms (I and II):



Form I
(Enol form)



Form II
(Keto form)

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[1] Not in the presence of other catalysts, cupric oxide, alumina, ferric oxide-alumina, and molybdic oxide-alumina.

[2] Tropsch, Third International Conference of Bituminous Coal, Pittsburgh, November, 1931.

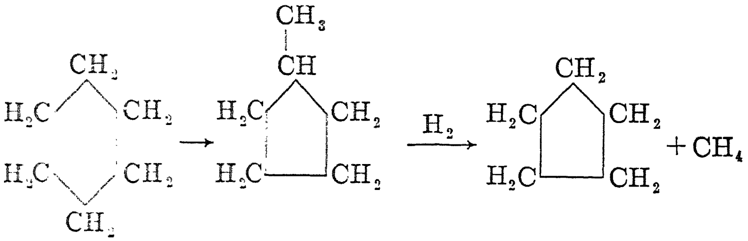
[3] Orloff, *loc. cit.*

[4] Kling and Florentin, Compt. rend., *182*, 526 (1926).

[5] Ipatieff, J. Russ. Phys. Chem. Soc., *38*, 89 (1906).

This explanation was confirmed by the following investigation. During hydrogenation, the real phenol (or enol form) is reduced to benzene with separation of water. This reaction proceeds at high temperatures (with other catalysts as well as with nickel oxide) or even under the influence of the iron walls of an autoclave. If a strong hydrogenating catalyst like nickel oxide is present, cyclohexane is the result of the hydrogenation. In the experiments on phenol the product consisted of 90% cyclohexane and 10% benzene, and separate experiments with cyclohexane showed that under these conditions the reaction is reversible.

It should be noticed that at 450 to 490° under high pressure in the presence of alumina, cyclohexane is isomerized to methylcyclopentane as shown first by Ipatieff and Dovgelevitch.[1] In the presence of hydrogen there is probably also decomposition of methylcyclopentane into methane and cyclopentane:



If another catalyst is used, the hydrogenation of the first tautomeric form of phenol gives only benzene. But in case hydrogenation of phenol is carried out with different catalysts (molybdic oxide, ferric oxide, nickel oxide), 10 to 30% of cyclohexane is always obtained. Its formation can proceed more easily by hydrogenation of the second tautomeric form of phenol, the ketone form, and for this purpose a less active catalyst could be used. The ketone form gives cyclohexanol which can easily give cyclohexane and its isomer methylcyclopentane.

The question also arises as to the effect of adding promoters such as alumina, thoria, etc., to the hydrogenation catalyst. On the basis of my early work (1910–1912) which showed for the first time the significance of the joint action of catalysts in heterogeneous catalysis, a particular function must be ascribed to these promoters. My recent experiments (unpublished) on the polymerization of olefins suggested a similarity between the action of alumina and of acids on olefins to the effect that olefins may combine with the meta hydrate of alumina (AlO(OH)) to form esters. Such esters would decompose into hydrocarbons in an activated state and consequently hydrogenation would occur at a lower temperature in the presence of the hydrogenating catalyst. Investigations of Ipatieff,[1] Tropsch,[2] and others showed that alumina which has not been heated too high and therefore contains water of hydration, is an active dehydration catalyst. This fact which has been established by many experimenters, is contradicted by the recent publication of Kling and Florentin,[3] who state that the best dehydrating catalyst is alumina which has been heated at 750°. They offer this high activity of alumina in explanation of the high yields of benzene obtained by high pressure hydrogenation of phenol at 490°. The last fact can be ascribed to a different cause, namely, that the highly heated alumina is incapable of promoting hydrogenation of the aromatic nucleus but plays the rôle of a porous substance so that only the reduction of phenol to benzene takes place.

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[1] Ipatieff and Dovgelevitch, Ber., *44*, 2987 (1911).

Special experiments on hydrogenation of aromatic hydrocarbons at high temperatures in the presence of originally active catalysts which had been poisoned by thiophene showed that single ring aromatic hydrocarbons cannot be hydrogenated. However, naphthalene can be hydrogenated in the presence of thiophene, as well as in its absence. Hydrogenation of phenol occurs in the presence of thiophene, but is accompanied by the formation of high boiling products, presumably esters.

The Hydrogenation of Monocyclic Aromatic Hydrocarbons

The hydrogenation was carried out in a rotating autoclave (of type described in 1904 [4]) at 260 to 450° in the presence of simple and mixed catalysts. The data are given in Table 93.

Experiments 4, 6, and 7 show that benzene cannot be hydrogenated in the presence of molybdenum catalysts. Under similar conditions xylene does not hydrogenate in the presence of molybdenum

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[1] Ipatieff, Ber., *37*, 2986 (1904).

[2] Tropsch, Third International Conference of Bituminous Coal, Pittsburgh, November, 1931.

[3] Kling and Florentin, International Conference of Bituminous Coal, Pittsburgh, November, 1931, page 1.

[4] Ipatieff, Ber., *37*, 2961 (1904).

TABLE 93

Expt. No.	Substance	Catalyst	Time, Hrs.	T., °C.	Press., Atms.		Anal. of Gas	Index of Ref.	Product of Reaction
					Start	End			
4	Benzene	MoO_3	3	430	100	99	H_2	1.5036/17	Benzene
6	Benzene	MoO_3, 50% Al_2O_3, 50%	3	400	65	65	H_2	1.5030/18	Benzene
7	Benzene	MoO_3, 50% Al_2O_3, 50%	3	450	65	64	H_2	1.5029/18	Benzene
9	Xylene	MoO_3	3	450	90	75	H_2, 95% Par, 5		Benzene Toluene Xylene
19	Xylene	MoO_3, 50% Al_2O_3, 50%	3	450	100	80			Benzene Toluene Xylene

catalysts, but decomposes to benzene and toluene (Expts. 9 and 19). The product of this reaction distilled from 80 to 140° and was entirely soluble in fuming sulphuric acid. By distillation it was separated as follows: (1) fraction boiling at 80–81° which solidified at 0°; (2) fraction boiling at 108–112° which by nitration formed dinitrotoluene. No naphthenes were found. Alumina at 430° gave the same results as the other catalysts (Expt. 35).

Hydrogenation of Naphthalene.—The experiments on the hydrogenation of naphthalene in the presence of different catalysts were carried out in the rotating autoclave at 450–475°. The data obtained are shown in Table 94. In Expt. 21 the mixed catalyst, nickel oxide (60%) and alumina (40%), was used. The products were identical with those obtained in a stationary autoclave by Ipatieff and Klukvin.[1]

Distillation of 133 g. of the hydrogenation product gave the following fractions: (1) 66–130° (16 g.); (2) 130–155° (18 g.); (3) 155–175° (19 g.); (4) 175–195° (20 g.); (5) 195–208° (50 g.); residue (naphthalene) (8 g.).

Fraction 5 (38% of the total product) boiling at 195 to 208° was tetrahydronaphthalene.

Anal. Calcd. for $C_{10}H_{12}$: C, 90.9; H, 9.1. Found: C, 90.8; H, 8.8.

Other fractions of the product contained the aromatic hydrocarbons, benzene, toluene, xylene, etc. In order to determine whether hydrocarbons other than aromatics were present, the different fractions were treated with 15% fuming sulphuric acid. These treatments showed the presence of naphthenes.

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[1] Ipatieff and Klukvin, Ber., *58*, 1–3 (1925).

TABLE 94

HYDROGENATION OF NAPHTHALENE

EXPT. No.	SUBS., G.	CATALYST	TIME, HRS.	T., °C.	PRESS., ATMS.			TETRALIN, % B.P., 195–208°	BENZENE HC, % B.P., 80–196°	NAPHTHENES, %		ANALYSIS OF GAS	
					Initial	End	Liquid			Fr. 80–120°	Fr. 120–150°	% H_2	% C_nH_{2n+2}
21	150	NiO, 60% Al_2O_3, 40%	11	450	100	39	133	38	47	15	10	81.0	14.5
17	150	MoO_3	12	450	100	42	110	28	53			78.0	17.2
18	150	MoO_3	12	450	100	47	130	28					
24	250	MoO_3	3	450	100	60	240	76	9	0	0		
25	250	MoO_3	10	475	100	38	205	Cryst.	47	10	0	41.2	58.8
8	100	MoO_3, 50% Al_2O_3, 50%	27	450	65	37	90	29				66.5	28.5
19	150		13	450	100	47	123	26	48			82.0	15.7
23	250		10	470	100	43	210	Cryst.	46	0	0	60.0	40.0
12	100	CuO, 50% Al_2O_3, 50%	28	450	65	40	64	10		0			
13	150		28	450	65	42							
9	50	Fe_2O_3, 50% Al_2O_3, 50%	19	450	65	52							
10	100		17	450	65	42							
11	100	Fe_2O_3, 50% Al_2O_3, 50%	42	450	65	34	142	Cryst.	22	0		70.0	26.3
26	250	Without catalyst	26	475	100	45	190	Cryst.	47	0		53.8	46.2

After treatment of the fractions boiling from 80 to 120° and 120 to 150° with fuming sulphuric acid, the hydrocarbons which remained did not react with nitrating mixture. In properties and analyses they corresponded to cyclohexane and its homologs. The hydrocarbon remaining after treatment of the first fraction with the fuming acid distilled at 76 to 104°; d^{0}_{4}, 0.7630; n^{21}_{D}, 1.4215.

Anal. Calcd. for C_nH_{2n}: C, 85.7; H, 14.3. Found: C, 85.8; H, 14.8.

Molybdic Oxide Catalyst.—In the hydrogenation of naphthalene at 450° in the presence of molybdic oxide alone with a short time of contact the yield of tetrahydronaphthalene increased to 76% (Expt. 24). When the time of hydrogenation was extended (Expts. 17 and 25) at 450–475° the percentage of benzene hydrocarbons increased considerably. The fraction boiling at 196 to 208° had d_{32} of 0.9360.

Anal. Calcd. for $C_{10}H_{12}$: C, 90.9; H, 9.1. Found: C, 90.5; H, 9.2.

Benzene hydrocarbons free from naphthenes were obtained in small amounts when the time of hydrogenation was short. When the hydrogenation treatment (Expt. 25) lasted a long time, the first fraction (80 to 120°) contained about 10% of naphthenes. After treatment of the first fraction with 20% fuming sulphuric acid, a hydrocarbon remained which did not react with nitrating mixture: b.p., 72–78°; d^{0}_{4}, 0.7547; n^{26}_{D}, 1.4070. The hydrocarbon was methylcyclopentane formed by isomerization of cyclohexane.

Anal. Calcd. for C_nH_{2n}: C, 85.7; H, 14.3. Found: C, 85.2; H, 14.8.

Molybdic Oxide (50%)-Alumina (50%) Catalyst.—This mixed catalyst gave the same results as did molybdic oxide (Expts. 8, 19, and 23). At 450°, 26–28% of tetrahydronaphthalene was formed. At 475°, very little tetrahydronaphthalene remained, since it decomposed forming gaseous paraffin hydrocarbons, principally methane. The fraction boiling at 196 to 208° had n^{20}_{D}, 1.5580.

Anal. Calcd. for $C_{10}H_{12}$: C, 90.9; H, 9.1. Found: C, 91.1; H, 8.4.

While but little tetrahydronaphthalene was obtained at 475°, the fraction boiling at 196 to 208° contained some naphthalene and therefore the amount of tetrahydronaphthalene remaining could not be determined. The aromatic hydrocarbon fractions did not contain other hydrocarbons.

Cupric Oxide (50%)-Alumina (50%) Catalyst.—With this catalyst also (Expts. 12 and 13) tetrahydronaphthalene was obtained but in yields of only 10%. Analysis of the fraction boiling at 200–208° and that boiling from 150 to 175°, showed the presence of tetrahydronaphthalene and aromatic hydrocarbons.

Analysis of fraction boiling from 150 to 175°: Calcd. for C_9H_{12}: C, 90.0; H, 10.0. Found: C, 90.1; H, 9.4.

Analysis of fraction boiling from 200 to 208°: Calcd. for $C_{10}H_{12}$: C, 90.9; H, 9.1. Found: C, 90.8; H, 8.7.

Ferric Oxide (50%)-Alumina (50%) Catalyst.—With this catalyst (Expts. 9–11) hydrogenation took place more slowly than with the preceding catalyst but tetrahydronaphthalene and aromatic hydrocarbons were formed.

Analysis of the different fractions gave the following results:

TABLE 95

Boiling Range, ° C.	Analysis, % Calcd.			Found	
	For	C	H	C	H
80–110	C_7H_8	91.3	8.7	91.0	8.8
125–150	C_8H_{10}	90.6	9.4	90.6	8.8
175–190	C_9H_{12}	90.0	10.0	89.6	10.0

Without Catalyst.—Experiment 26 showed that at 475° in the absence of a catalyst the hydrogenation of naphthalene followed the same course as in the presence of different catalysts, but that the rate of reaction was much slower. Small amounts of tetrahydronaphthalene and aromatic hydrocarbons were the only products of the decomposition of tetrahydronaphthalene.

The Influence of Thiophene upon the Hydrogenation of Naphthalene.—Tests were made on the hydrogenation of naphthalene in the presence of thiophene in order to determine the influence of poisoning upon hydrogenation at temperatures low enough to avoid decomposition of the hydrogenated products first formed. At high temperatures thiophene had no appreciable effect upon the hydrogenation reaction. Thus the hydrogenation of naphthalene in the presence of nickel oxide-alumina catalyst produced 38% of tetrahydronaphthalene while in the presence of thiophene the yield of this product was 33%.

Expt. No.	Catalyst	Time, Hrs.	T., °C.	Press., Init.	Atms., End	HC, %	Analysis of Hydrocarbon Fractions					
							Distillation		Index of Refraction		Specific Gravity	
									26°		26°	
							I	II	I	II	I	II
7	NiO, 50%	25	400	80	20	95	77-83		1.4441			
8	Al_2O_3, 50%	2	450	64	20	93	75-78	78-81				
12	MoO_3, 50%	2	425	65	35	88	70-77	77-82	1.4642	1.4789	0.8125	0.8291
13	Al_2O_3, 50%	2	450	65	35	92	70-78	78-82	1.4671	1.4679	0.8155	
10	Al_2O_3, 50%	3	475	65	35	95	70-78	78-82	1.4679	1.4840		
16	MoO_3	2	450	65	31	83	69-81	81-88		1.4650		
17	MoO_3	2	450	65	35		70-79	79-83				
22	Fe_2O_3, 50%	2	450	65	55	22	75-82	82-84	1.4815	1.4362		
23	Al_2O_3, 50%	2	450	65	57		70-72	72-81	1.4430	1.4750	0.8337	
20	Without	2	450	65	52	25	75-81	81-84	1.4730	1.4935	0.8454	
21	catalyst	2	450	65	53							
25	Al_2O_3	2	450	65	57	10	70-84		1.4755			
27	Al_2O_3	2	450	65	58	8						

Hydrogenation of Phenol.—The hydrogenation of phenol proceeded under the same conditions as described in the case of naphthalene. The data are summarized in Table 96.

TABLE 97

Expt. No.	Phenol (100 g.) Analysis of Hydrocarbon Fractions I and II after Treatment with Fuming H_2SO_4 (20%)						Product of Destr. Hydrogenation Contained, %		Analysis of Gas	
	Distillation		Index of Refraction 26°		Specific Gravity 26°					
	1	2	1	2	1	2	Benz. HC	Cyclohexane	% H_2	% C_nH_{2n+2}
7	75–84		1.4248				10	90	96	1.6
8	75–84		1.4246				12	88	96	1.8
12	75–77		1.4163				88	12		
13	74–77	81–83	1.4140	1.4244	0.7583		84	16	94.6	1.2
10	74–77	81–83	1.4230				85	15		
16	75–76	79–80	1.4189	1.4240	0.7504	0.7620	70	30		
17		79–80		1.4215	0.7326		80	20	93.8	1.8
22	75–82		1.4230				84	16	94.3	4.0
23	75–82		1.4283				84	16		
20	77–79	79–81	1.4249	1.4270	0.7634		80	20	94.4	3.9
21										
25	75–82		1.4186				88	12		
27										

$NiOAl_2O_3$—The precipitation (nitrate salts) was made by addition of ammonium carbonate. The product was dried 17 hours at 210° and in a stream of air for 5 hours at 400°. All catalysts were used in amount of 10% of the substance.

Catalyst NiO (50%) and Al_2O_3 *(50%).*—Experiments 7 and 8 showed that hydrogenation begins at 400°. In Experiment 7 when the temperature was 260°, the pressure did not drop for 22 hours; only when the temperature was increased to 400° did the reaction proceed. After 2 hours of heating, 95% of the reaction product consisted of hydrocarbons which, after thorough treatment with 15% fuming sulphuric acid at 0°, left 90% cycloparaffins (cyclohexane and methylcyclopentane), as the product of isomerization. With an active catalyst, phenol was hydrogenated to cyclohexanol, which in turn was transformed into cyclohexane. The reduction of phenol directly to benzene occurred only to a small extent.

Catalyst MoO_3 *(50%) and* Al_2O_3 *(50%).*—As seen from Expts. 12 and 13, phenol at 450–475° in the presence of hydrogen gave almost a 90% yield of hydrocarbons. By distillation, the following fractions were obtained: (1) 70–77°, d_4^{26}, 0.8125, n_D^{26}, 1.4679; (2) 77–82°, d_4^{26}, 0.8291, n_D^{26}, 1.4840; (3) 82–100°; (4) 100° (12 g.).

Treatment of the fraction boiling at 70–77° with fuming sulphuric acid (15%) [1] resulted in a hydrocarbon boiling at 75–77°;

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[1] The last trace of aromatic hydrocarbons was difficult to remove with 15% fuming sulphuric acid; therefore, it was necessary to repeat the treatment with 30% fuming sulphuric acid at 0°.

n_D^{26}, 1.4163. Treatment of the fraction boiling at 77–82° with 15% sulphuric acid gave a hydrocarbon boiling at 78–80°; n_D^{26}, 1.430.

The same results were obtained in Expt. 13.

Analysis of the fractions, after treatment with sulphuric acid, gave the following results:

Anal. Calcd. for C_nH_{2n}: C, 85.6; H, 14.4. Found: Fraction 74–77°: C, 85.4; H, 14.4. Fraction 81–83°: C, 84.9; H, 14.6.

The hydrocarbon products did not react with nitrating mixture and according to their analysis and properties they were mixtures of cyclohexane and methylcyclopentane.

Molybdic Oxide (MoO_3) Catalyst.—This catalyst gave the same picture of hydrogenation as in the preceding cases, but as it was a more active catalyst the amount of naphthenes obtained was slightly greater (Expts. 16 and 17).

An analysis of the fractions gave the following results:

Anal. Calcd. for C_nH_{2n}: C, 85.7; H, 14.3. Found: Fraction 73–76°: C, 85.0; H, 14.7. Fraction 79–86°: C, 84.9; H, 14.6.

Ferric Oxide (50%) and Alumina (50%) Catalyst.—The amount of phenol decomposed with this catalyst was considerably less, about 25% (Expts. 22 and 23). The hydrocarbon fractions obtained after distillation had high indices of refraction which indicated that little cyclohexane was present. After treatment with 15% fuming sulphuric acid, about 16% of cyclohexane remained with n_D^{26} 1.4230.

No Catalyst.—When phenol was hydrogenated without a catalyst (Expts. 20 and 21) almost the same results were obtained as in the preceding experiment with the iron oxide catalyst. In this case the iron walls of the autoclave acted catalytically and the phenol was hydrogenated to produce about 20% of cyclohexane.

After treatment of the fractions boiling at 77–79° and 79–81° with 15% fuming sulphuric acid, a hydrocarbon was obtained which did not react with nitrating mixture and which according to analysis and properties was cyclohexane.

Anal. Calcd. for C_6H_{12}: C, 85.6; H, 14.4. Found: C, 84.9; H, 14.6.

Alumina (100%).—The amount of hydrocarbon fraction decreased in the presence of alumina (Expts. 25 and 27). The formation of unsaturated hydrocarbons, probably hexenes, also became noticeable as shown by the fact that the resulting hydrocarbons decolorized alcoholic potassium permanganate solution. After treatment with 15% fuming sulphuric acid, a hydrocarbon was obtained which did not react with nitrating mixture. It was a mixture of cyclohexane and methylcyclopentane, a result in accord with the experiments of Ipatieff and Dovgelevitch on the isomerization of cyclohexane into methylcyclopentane under the influence of alumina. By destructive hydrogenation of phenol in the presence of different catalysts, high boiling fractions also were obtained. These fractions boiling at 220–280° contain presumably phenyl ether and cyclohexylcyclohexanol.

Hydrogenation of Phenol in the Presence of Thiophene. Molybdic Oxide (MoO_3) Catalyst.—The results were the same as those above when phenol containing 1% of thiophene was hydrogenated in the presence of molybdic oxide under similar conditions. Two hundred grams of phenol hydrogenated at 450° for two hours yielded 160 g. of a product which contained only 12 g. of unreacted phenol. The rest of the product distilled at 69–84°.

TABLE 98

Fraction	Boiling Range, °C.	d_0^{24}	n_D^{23}
1	69–81	0.8068	1.4580
2	81–84	0.8229	1.4680

These fractions gave no reaction for thiophene and did not decolorize an alcoholic potassium permanganate solution.

After the two fractions were treated with 15–20% fuming sulphuric acid, 26% of hydrocarbon remained having the following characteristics:

TABLE 99

Fraction	Boiling Range, °C.	n_D^{24}
1	72–77	1.4200
2	77–81	1.4230

The resulting hydrocarbon did not react with nitrating mixture and it probably was cyclohexane mixed with a small amount of methylcyclopentane.

Nickel Oxide (50%) and Alumina (50%) Catalyst.—In the presence of this catalyst, 200 g. of phenol containing 1% of thiophene was hydrogenated at 450° during 2 hours. The 170 g. of product obtained distilled as follows:

TABLE 100

Fraction	Boiling Range, °C.	d_0^{24}	
1	69–75	0.7693	1.4228
2	75–84		1.4330
3	84–86		1.4350

The hydrocarbon did not decolorize potassium permanganate solution and consisted presumably of cyclohexane containing a small amount of benzene. In the absence of thiophene, the yield of hydrocarbon was 90 to 95% of the theoretical, but in this case, the hydrocarbon yield was 50%, the remainder of the reaction product consisting of unreacted phenol. High boiling products were formed also: (1) 150–175° (1 g.); (2) 175–215° (3 g.); (3) 215–240° (4 g.); (4) 240–260° (4 g.); (5) 260–290° (6 g.); (6) 290–330° (4 g.); (7) 330–360° (3 g.); Bottoms (4 g.).

To determine the nature of these products, fractions 4 to 6 were treated with 25% sodium hydroxide solution and analyzed. The analyses showed that they contained oxygen. Therefore, it may be inferred that these products consisted of phenyl ether and cyclohexylcyclohexanol.

Conclusions

(1) Hydrogenation of monocyclic aromatic hydrocarbons does not take place in the presence of molybdenum catalysts prepared in the usual way by precipitation.

(2) During destructive hydrogenation with catalysts, the combination of hydrogen with aromatic compounds occurs first, followed by the decomposition of the hydrogenated product.

(3) Active catalysts may hydrogenate a benzene ring at the time of its formation and during the decomposition of the hydrogenated product of a polynuclear aromatic hydrocarbon.

(4) The destructive hydrogenation of phenol is due to its tautomeric form.

(5) The presence of thiophene does not change the rate of the destructive hydrogenation of naphthalene.

(6) The presence of thiophene decreases the yield of hydrocarbons obtained from phenol by hydrogenation.

(7) Thiophene decomposes completely under these conditions.

DESTRUCTIVE HYDROGENATION OF AROMATIC COMPOUNDS UNDER THE INFLUENCE OF MIXED CATALYSTS [1]

The influence of high temperatures on the decomposition of various organic compounds had already been studied by many investigators. Here it will be sufficient to mention the work of Berthelot, Barbier, Kraemer, Spilker, and Engler. In many cases, in order to start the reaction, it was necessary to raise the temperature considerably beyond the point at which the primary products of decomposition could exist. Thus a whole series of by-products were observed as a result of side reactions starting with the fragments of the primary products. The decomposition process is often so intense that the products of pyrolysis consist mostly of free carbon; the hydrogen liberated in this case combines with fragments of the initial substance. This phenomenon has a special significance in the case of pyrolysis under pressure.

The decomposition or dissociation of organic substances may lead to the formation of numerous fragments of the primary molecule or it may have the tendency to form multiple bonds within the molecule itself. Furthermore, the fragments may unite to form new molecules. The hydrogen liberated during decomposition may either add to these fragments or radicals, or saturate the unsaturated bonds formed, giving saturated or stable unsaturated compounds. On the other hand, with the formation of new molecules from the fragments of the original substance, processes of polymerization take place and are often observed in technical pyrogenetic processes. However, the experiments of Ipatieff and Klukvin [2] showed that the formation of condensation and polymerization products was avoided to a considerable extent when the decomposition of organic substances was carried out under hydrogen pressure. In this case, the fragments of the initial substance add hydrogen immediately and form simple molecules, thus avoiding the formation of polymers. Besides this, it is necessary to consider the fact that in the presence of hydrogen and especially under pressure (as was shown in 1901–1904 in the study of the decomposition of organic substances) the walls of the vessel in which the process is conducted act catalytically. The iron walls of the autoclave serve as catalyst which assists in the hydrogenation of the free radicals as well as of unsaturated compounds. It was decided to study the decomposition of aromatic compounds at temperatures of 500° or lower in the presence of a catalyst which would not hydrogenate the aromatic nucleus under high pressure.

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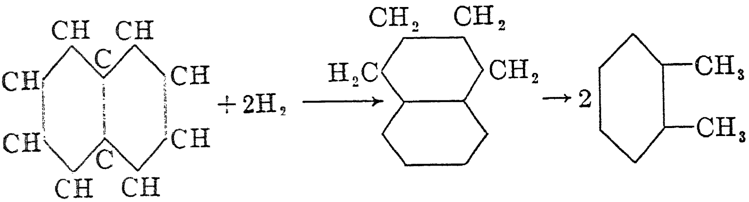
[1] This work was carried out together with Orloff; Ber., *60*, 1963 (1927).

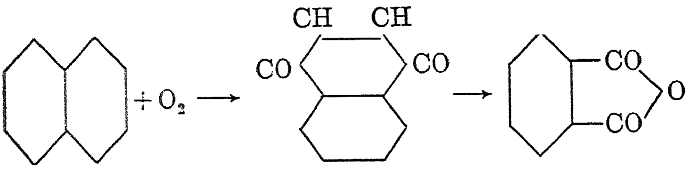
[2] Ipatieff and Klukvin (refer to above).

A catalyst which may cause such a decomposition is a *mixed catalyst* consisting of *alumina* and *iron* (the walls of the autoclave). As previously shown, alumina has the ability of lowering the temperature of decomposition of organic compounds.

In order to form new simple molecules from the fragments (radicals) of the primary molecule, it is necessary to add hydrogen to them. For this purpose, the assistance of a second catalyst, iron, is necessary. If a more active catalyst such as nickel is used for the hydrogenation (as shown by my experiments with Klukvin on naphthalene), one aromatic nucleus is hydrogenated, after which the hydroaromatic (naphthenic) nucleus opens and a series of aromatic hydrocarbons such as benzene, toluene, and o-xylene results.



It is interesting to note that when oxygen and an oxidation catalyst is used [1] in the decomposition of naphthalene, naphthoquinone and phthalic anhydride are obtained.



Among the many substances subjected to destructive hydrogenation and studied in detail were the following: *diphenyl ether, phenol, o-cresol, catechol, aniline, triphenylmethane, diphenylmethane, tetralin, diphenyl, acenaphthene, anthracene, mesitylene,*

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[1] Mayer, Chem. Zeit., 47, 213 (1923).

solvent naphtha, and *heavy coal tar oil.* All experiments were carried out in high pressure apparatus having capacities of from 250 to 1100 cc. The initial pressure of hydrogen was 70 atmospheres; the amount of the substance used in the experiment varied from 20 g. to 70 g., and the catalyst was a mixture of *aluminum oxide* with *iron, copper* or *copper oxide.* For all the substances mentioned, the temperature of the experiments was not lower than 400°.

Phenyl Ether.—Phenyl ether, $C_6H_5—O—C_6H_5$, is a very stable compound. At 250°, it is not decomposed either by hydroiodic acid or by zinc dust. Partial decomposition occurs if it is heated under approximately 60 atmospheres of pressure for 4–5 hours at 500–530° (not with hydrogen). This treatment leaves 65% of phenyl ether undecomposed; and there is formed about 3% of phenol, traces of benzene, a small amount of a combustible gas, and a residue consisting of a thick, black tar which distills without decomposition.

By heating phenyl ether for 4 hours at 480° in the presence of alumina and iron, 9% of phenol and 15.3% of benzene were obtained.

$$C_6H_5—O—C_6H_5 + H_2 \rightarrow C_6H_5OH + C_6H_6$$

The phenyl ether remaining undecomposed did not show any formation of tar and had acquired only a slight yellowish fluorescence. When *copper oxide* was added to the alumina, the temperature of the decomposition could be decreased to 450°.

Phenol.—The fact that the yield of phenol in the preceding experiment did not correspond to that of the benzene (refer to equation written above) indicated that phenol was converted into benzene under these conditions. As is known, F. Fischer [1] observed the conversion of phenol into benzene at 700°. In the absence of hydrogen, phenol is changed slightly by heating up to 500° in high pressure apparatus; small amounts of diphenylene oxide and phenyl ether [2] are formed. Heating phenol 4 hours with a mixture of alumina and copper oxide resulted in the formation of 20% of the theoretical amount of benzene, the remaining phenol undergoing not the slightest resinification.

o-Cresol.—Under experimental conditions similar to those used with phenol, o-cresol gave 30% of a mixture of benzene and toluene and an insignificant quantity of resinification products.

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[1] Fischer, "Conversion of Coal into Oils" (1926).

[2] Ipatieff, Orloff, and Petrov, Ber., *60*, 130 (1927).

Catechol.—Catechol heated 4 hours with hydrogen in the presence of a mixed catalyst under conditions similar to those previously indicated, gave a product consisting of 10% benzene, 75% of very pure phenol, and 15% of a brown tar.

Aniline.—Aniline is a very stable compound at high temperatures. By passing aniline vapors through a glowing tube, Hoffmann [1] obtained a complex mixture of substances consisting of *ammonia, hydrogen cyanide, benzene, benzonitrile,* and *carbazole.* Aniline heated under pressure of its own vapors at 500° underwent almost no change; there was a slight resinification and only traces of *diphenylamine* and *ammonia* were formed. When hydrogenated, according to the method of Sabatier and Senderens,[2] aniline decomposes partially, forming cyclohexane and ammonia. It is possible that under these conditions cyclohexylamine is formed first, but being unstable decomposes into the compounds indicated. My experiments on the hydrogenation of aniline under pressure gave much better results because of the restriction imposed on the decomposition of cyclohexylamine. On the other hand, there is recorded an experiment [3] on the hydrogenation of aniline under hydrogen pressure developed by the action of iron on acetic acid in which the greater part of the aniline decomposes into benzene and ammonia.

The reaction of aniline with hydrogen under pressure in the presence of alumina proceeds similarly. By heating at 440–470° for $3\frac{1}{2}$ hours, aniline gave 23% of the theoretical amount of *benzene* and *ammonia* and a small amount of *diphenylamine.* The aniline remaining contained a little tar. The reaction is reversible to a certain extent since traces of aniline are formed by heating benzene and aqueous ammonia under pressure in the presence of a catalyst.

Triphenylmethane.—By hydrogenating triphenylmethane under pressure, Ipatieff and Dolgoff [4] obtained dicyclohexylmethane and dicyclohexyl in addition to the normal product, tricyclohexylmethane. In all probability the cyclohexyl radical broke away from the completely hydrogenated hydrocarbon; however, it is also possible that the phenyl radical split from the original hydrocarbon. Saturated gaseous hydrocarbons were found in the products after 25 g. of triphenylmethane had been heated 6 hours at 500° in the presence of alumina under an initial hydrogen pressure of 60 atmospheres. The liquid product of the reaction contained 10 g. of benzene and 1 g. of a fraction boiling at 260–270° which solidified on cooling. From its analysis, properties, and orange-like odor, it was considered to be *diphenylmethane.*

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[1] Hoffmann, Jahresbericht, 335 (1862).
[2] Sabatier and Senderens, Compt. rend., *138*, 457 (1904).
[3] Scheurer-Kestner, Bull. soc. chim., *4*, 43 (1862).
[4] Ipatieff and Dolgoff, J. Russ. Phys. Chem. Soc., *57*, 1023 (1926).

Anal. Calcd. for $C_{13}H_{12}$: C, 92.8; H, 7.2. Found: C, 92.7; H, 7.2.

When the residue in the flask was dissolved in benzene, a complex of triphenylmethane and benzene, slightly soluble in benzene, crystallized.

Pure *diphenylmethane* was considerably more stable under similar conditions; 6 hours of heating led to the formation of 6–7% of benzene.

Tetralin.—This compound, when heated with hydrogen at 480° for 4–5 hours in the presence of a catalyst, underwent a decomposition which was completely analogous with that of naphthalene.[1] About 30% of the tetralin remained undecomposed; 30% was converted into naphthalene, and 40% into a mixture of aromatic hydrocarbons distilling at 80–200°.

Diphenyl.—Orloff's [2] experiment showed that diphenyl gave almost a 50% yield of benzene when heated at 500° under hydrogen pressure for 4½ hours in the presence of a mixed catalyst consisting of alumina and copper oxide. Only unchanged diphenyl remained after the benzene was distilled from the product.

Acenaphthene.—It was to be expected that the decomposition of acenaphthene under our conditions would produce ethylene and naphthalene since acenaphthene has been synthesized pyrogenetically from these substances. However, on heating acenaphthene with alumina and copper oxide in the presence of hydrogen at 450–470° the resulting product consisted of *naphthalene* and a liquid product distilling between 80–200°. This liquid consisted of aromatic hydrocarbons, the formation of which must be ascribed to the decomposition of naphthalene in the presence of hydrogen. In addition to hydrogen, a small amount of saturated hydrocarbons was also present in the gaseous product of the reaction.

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[1] Ipatieff and Klukvin, Ber. (1926), *loc. cit.*
[2] Orloff, Ber., *60*, 1950 (1927).

Anthracene.—Anthracene, when heated with hydrogen under pressure, proved to be a most unstable compound. The chief product resulting from this reaction was coke. After heating 100 g. of anthracene for 8 hours at 480°, about 30 g. of thick, brown liquid was obtained, which was not investigated. The remainder of the anthracene was converted into a mass of porous coke. The gases contained saturated hydrocarbons.

Mesitylene.—From 35 g. of mesitylene (b.p., 161–164°) after 6 hours heating at 460°, 2 g. of aromatic hydrocarbons were obtained which distilled at 100–150°. These aromatic hydrocarbons consisted of a mixture of toluene and xylenes originating from mesitylene by demethylation. The remainder of the product was unchanged mesitylene.

Our experiments showed that the destructive hydrogenation of aromatic hydrocarbons under pressure takes place at relatively low temperatures in the presence of certain catalysts, and that it leads to the formation of simpler molecules. The addition of hydrogen to certain parts of the molecules of complex aromatic compounds makes them less stable so that they decompose. An excess of hydrogen assists in the formation of definite compounds composed of fragments of the decomposed hydrogenated product. This action of hydrogen may be considered analogous to the action of aluminum chloride in forming at the beginning of a reaction unstable complexes which either decompose more readily than the initial substance, or (as will be seen later in the chapter on alkylation) enter more readily into a chemical reaction with other substances. Because of these ideas, it was decided to conduct experiments on destructive hydrogenation not only with individual hydrocarbons, but also with the commercial products, *solvent naphtha* and *heavy coal tar oil*, with the expectation of decomposing them into benzene and its simple derivatives so important in present-day life. As will be seen below, these expectations were realized.

Solvent Naphtha (from Coal Tar).—By repeated fractionation of solvent naphtha, a fraction was obtained boiling between 146 and 200°. In a high pressure apparatus of 800 cc. capacity this product (in 60 g. portions) was heated for 9 hours at 480–500° in the presence of a mixture of alumina and copper oxide under 60 atmospheres initial hydrogen pressure. After cooling, the pressure decreased slightly. Gas analysis indicated the presence of about 20% of saturated hydrocarbons in the gas.

From a total of 180 g. of solvent naphtha, 135 g. of a pale yellow, green fluorescent liquid was obtained. The following fractions were separated by two distillations: (1) 80–115° (25 g.); (2) 115–140° (55 g.); (3) 140–190° (40 g.); residue (8 g.).

All fractions dissolved completely in fuming sulphuric acid. They were subjected also to the action of nitrating mixture. In the first fraction, the presence of benzene was proved according to the method of Hoffmann and Arnoldi [1] by means of nickel cyanide. Five grams of this fraction gave, after treatment with the cyanogen reagent, 0.7622 g. of complex compound which corresponded to 0.2055 g. of benzene. Consequently, the first fraction contained 4.1% benzene. After washing and drying, the hydrocarbon which did not react with the cyanogen reagent had a boiling range of 109–114° and after repeated nitrations gave trinitrotoluene with a melting point of 79°.

The second fraction evidently consisted of toluene mixed with xylenes or ethylbenzene, since the analysis gave the following data:

Anal. Calcd. for C_7H_8: C, 91.3; H, 8.7. Calcd. for C_8H_{10}: C, 90.6; H, 9.4. Found: C, 91.0; H, 8.9.

Oxidation of the second fraction with potassium permanganate solution produced a considerable amount of benzoic acid. The distillation residue consisted chiefly of naphthalene and a very small amount of tarry products.

The third fraction consisted apparently of unchanged starting material and a small amount of phenol, which was not present in the original product. This phenol could have originated from decomposition of the *cumarone* present in the original substance.

Heavy Coal Tar Oil.—A fraction boiling at 260–300° (free from naphthalene) was separated from the heavy coal tar oil and used in the following experiment. The oil after distillation was slightly yellow in color, darkened rapidly on exposure to air, and had an odor resembling that of hydrogen sulphide. Its specific gravity was d_0^{25}, 1.062. Altogether a total of 250 g. of material was processed, each experiment being with 50 g. This oil was heated at 415–435° for 15 to 17 hours under 70 atmospheres initial hydrogen pressure in the presence of a 50/50 mixture of aluminum and iron oxides. After cooling, the pressure in the apparatus was less than the initial. The residual gas consisted of hydrogen, paraffins, and ammonia. The liquid product (180 g.) was brown. It did not have the odor of sulphur compounds. The following fractions were obtained by distillation: (1) 50–100° (7 g.); (2) 100–150° (45 g.); (3) 150–200° (8 g.); (4) 200–250° (55 g.); (5) 250–260° (10 g.); (6) 260–340° (45 g.). The first fraction contained *benzene* and light gasoline. After treating with sulphuric acid a layer of light hydrocarbons remained (4% of the product). The second fraction consisted chiefly of *toluene* and *xylene* which were oxidized by potassium permanganate solution to a mixture of benzoic and o-phthalic acids. The third fraction was not studied because of the very small quantity available.

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[1] Hoffmann and Arnoldi, Ber., *39*, 339 (1906).

The fourth fraction presented the greatest interest. After repeated distillation, 42 g. (17% of the starting oil) of pure *naphthalene* was obtained. The origin of the naphthalene might be attributed to the removal of side chains from the substituted naphthalenes present in the original oil. The destructive hydrogenation of naphthalene leads to the formation of mono- and disubstituted benzenes. By shortening the time of the reaction it may be possible to increase the yield of naphthalene.

The fifth and sixth fractions contained unchanged oil mixed with higher boiling products which solidified at room temperature to a semi-solid material which was probably a polymerization product.

The data presented above show that destructive hydrogenation of aromatic compounds not only makes it possible to study the various directions of the decomposition of complex molecules, but it also has technical interest. Doubtless, better yields of desired products could be obtained in a continuous rather than batch process. The correct contact time could be employed and the products would be continuously removed from the system. Very likely the reaction could be run at a lower temperature than used in my experiment.

DECOMPOSITION OF HEXANE AND CYCLOHEXANE UNDER PRESSURE[1]

Before further discussion of the investigations on destructive hydrogenation under pressure, it is considered sufficiently important to mention the first experiments on the decomposition of the simple organic compounds, hexane and cyclohexane, under pressure and without hydrogen.

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[1] Ipatieff and Dovgelevitch, Ber., *44*, 2987 (1911).

Ordinary Pressure.—Experiments were made on the decomposition of hexane and cyclohexane without pressure in order to compare the decomposition behavior of these compounds.

Hexane (b.p., 66–68°) was obtained by fractionation of commercial hexane from Kahlbaum. Cyclohexane (b.p., 80–80.5°), free from traces of benzene, was obtained by the hydrogenation of benzene under pressure. The hydrocarbons were passed through a heated iron tube which was sometimes empty, sometimes filled with catalyst. The results of these experiments appear in the following table:

TABLE 101

Substance	Weight of Substance, G.	Catalyst	T., °C.	Time, Hrs.	Liters	Gas Produced, Analyses			Liquid Product, G.	B.P., °C. of Liquid Product
						% C_nH_{2n}	% H_2	% C_nH_{2n-2}		
Hexane	90		710	2.0	17	50.	8.4	41.6	67	37–72
Hexane	100	Al_2O_3	660	2.5	34	47.6	8.4	44.0	46	36–74
Cyclohexane	65	Al_2O_3	740	1.0	13	46.8				
Cyclohexane	65		750	1.0	12	44.5	14.0	42.0	39	42–87
Cyclohexane	65	Zn dust	730							
Cyclohexane	65	Reduced Cu	730						35	38–84

As seen from the table, the decomposition of hexane and cyclohexane requires high temperature (650–700°). Hexane decomposes more readily than cyclohexane and alumina hastens the reaction. The gas obtained by the decomposition of hexane and cyclohexane was passed into bromine. On the basis of analysis of the resulting bromides, it was concluded that in addition to saturated hydrocarbons, the gaseous products contained ethylene, propylene, and perhaps isobutylene.

The liquid products obtained by the decomposition of the two hydrocarbons contained insignificant amounts of unsaturated hydrocarbons which were readily removed by sulphuric acid (sp. gr., 1.84). The remaining hydrocarbons (insoluble in sulphuric acid) did not react with nitrating mixture nor with potassium permanganate solution.

High Pressure.—The decomposition of hexane and cyclohexane was carried out in a high pressure apparatus as follows: Forty grams of hydrocarbon and 3 g. of alumina were placed in the tube, and a temperature of 500–510° was maintained for 4 hours during which time the pressure rose to 100–120 atmospheres. After cooling, the pressure in the apparatus was 15 atmospheres and the gas produced amounted to 3.5 to 4 liters. Although it seemed desirable to obtain more liquid decomposition products, it appeared irrational to prolong the time of heating because this factor would increase the volume of gas formed.

Decomposition of cyclohexane did not take place at this temperature in the absence of alumina. Therefore, with cyclohexane, alumina acted as a decomposition catalyst. In this experiment, 700 g. of cyclohexane yielded 400 g. of liquid product. The average composition of the gas was 3.8% of olefins, 22.4% of hydrogen, and 73.5% of methane.

The liquid product was separated by distillation into the following fractions: (1) 45–65°; (2) 65–75°; (3) 75–85°; (4) 85–100°; (5) 100–130°; (6) 130–150°; (7) 150–200°; (8) 215–250°; (9) 250–295°; (10) 295–310°.

All fractions decolorized potassium permanganate solution and reacted with nitrating mixture and the higher the boiling point of the fraction, the more vigorous the reaction with nitrating mixture. Thus, fractions 8, 9, and 10 immediately liberated oxides of nitrogen on treatment with nitrating mixture.

All fractions were treated with sulphuric acid (*d*,1.84) to remove unsaturated hydrocarbons, and it was estimated that the approximate olefin content [1] in the various fractions ranged from 5 to 10%. They were redistilled after the removal of the olefins, and nine fractions were obtained having the same boiling ranges as before treatment with sulphuric acid. These fractions had the properties and analyses shown in Table 102.

None of the fractions decolorized potassium permanganate solution. The first four fractions did not react with nitrating mixture, but the fractions distilling at 100–120° reacted energetically thus indicating with certainty the presence of aromatic hydrocarbons. The first three fractions were free from paraffin

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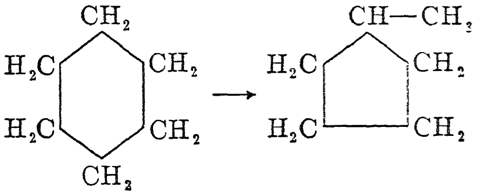
[1] Because of the presence of aromatic hydrocarbons in all fractions, the content of olefins could not be determined accurately by means of sulphuric acid. (Refer to chapter on alkylation.)

TABLE 102

Fraction No.	B.P., °C			Substance, G.	CO_2, G.	H_2O, G.		H
1	45– 65	0.7471	1.40752	0.1138	0.3698	0.1540	85.21	14.47
2	65– 77	0.7535	1.40882	0.1744	0.5448	0.2266	85.19	14.44
3	75– 80	0.7643	1.41383	0.1739	0.5428	0.2256	85.56	14.48
4	79– 82	0.7738	1.41655	0.1400	0.4428	0.1686	86.28	13.38
5	92–105	0.7870	1.43096	0.3227	1.0332	0.3766	87.32	12.96
6	125–150	0.8255	1.44010	0.1881	0.5962	0.2208	86.44	13.02
7	150–170	0.8602	1.44800	0.1981	0.6350	0.2250	87.41	12.62
8	210–250	0.9017	1.49182	0.1958	0.5388	0.1956	88.92	11.08
9	250–280	0.9363	1.52272	0.2176	0.7420	0.1992	90.74	10.17

hydrocarbons as shown by their carbon-hydrogen percentages which corresponded closely to that of naphthenic hydrocarbons.[1]

The analyses and properties of the first three fractions indicated that they contained not only undecomposed cyclohexane, but also a considerable quantity of another hydrocarbon isomeric with it, namely methylcyclopentane, formed by isomerization of cyclohexane under the influence of the alumina catalyst.



Such isomerization was confirmed by later investigation. (Refer to chapter on "Catalytic Isomerization.")

In view of its analysis and its energetic action with nitrating mixture, it may be assumed with certainty that fraction 6 contained aromatic hydrocarbons. From this fraction a nitro product was isolated which melted at 160–163° and from fraction 7 a nitro product was obtained which melted at 148–150°.

It is to be inferred that polynuclear as well as saturated hydrocarbons were present in the higher fractions since they were richer in carbon and had higher boiling points. Thus, for example, fraction 9, according to its carbon and hydrogen content, should correspond to xylene, but its boiling point indicates that a polynuclear hydrocarbon is present.

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[1] These fractions did not contain benzene. But according to recent investigations it cannot be stated that benzene was not present in the corresponding fractions of the decomposition products before treatment with sulphuric acid.

DESTRUCTIVE HYDROGENATION OF AROMATIC COMPOUNDS UNDER HYDROGEN PRESSURE IN THE PRESENCE OF A MIXED CATALYST [1]

Previous study [2] had shown that the decomposition of a number of aromatic compounds in the presence of hydrogen under pressure led to the formation of lower boiling products richer in hydrogen than the starting material. In these experiments the alumina catalyst lowered the decomposition temperature to such an extent that this reaction took place at 450–480° under about 200 atmospheres pressure. After the destructive hydrogenation of individual compounds had been studied, this reaction was applied to technical products such as solvent naphtha and others. These experiments gave satisfactory results and indicated the possibility of obtaining low boiling products and aromatic hydrocarbons from heavy oils and tars. Simultaneously, it was found that much naphthalene was formed by the decomposition of heavy coal tar.

The present investigation was undertaken in order to test experimentally our explanation of the formation of naphthalene from substituted naphthalenes present in the initial product. It was also of interest to solve the question concerning the formation of a small amount of benzene in the destructive hydrogenation of heavy coal tar. The simplest explanation is that it originates through the decomposition of paraffins present in the oil.

The formation of ammonia by decomposition of heavy oil in the presence of hydrogen suggested more thorough investigation of the decomposition of organic bases under the conditions indicated inasmuch as preceding experiments showed that aniline decomposes into benzene and ammonia with great ease.

Quinoline and carbazole (which have different decomposition temperatures) were chosen as the substances to be studied. Carbazole, present in coal tar, has a structure similar to that of diphenyloxide. Carbazole, and diphenyloxide as well, are very stable compounds, undergoing almost no change under the conditions of the experiment.

The formation of light hydrocarbons from solvent naphtha was shown by earlier experiments to be due to "dealkylation" of the homologs of benzene. It was interesting to follow the fate of the other components of solvent naphtha, particularly indene. Experiments showed that with sufficiently high hydrogenation pressure, indene can be converted into hydrindene which decomposes into substituted benzenes. But with low pressures of hydrogen, indene is converted almost completely into a thick tar which decomposes on distillation.

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[1] Ipatieff and Orlow, Ber., *62*, 593 (1929).

[2] *Ibid.*, *60*, 1963 (1927).

Experiments on the decomposition of tetralin described in previous pages were repeated under modified conditions in which tetralin was decomposed under pressure of its own vapor without the addition of hydrogen. In this case its hydrogenated nucleus was destroyed with the formation of benzene hydrocarbons and simultaneous dehydrogenation was observed with the formation of high boiling hydrocarbons.

The marked stability of diphenylmethane, a substance detected in previous experiments, induced us to make experiments with diphenylethane (dibenzyl), related to it in many respects. It was found that dibenzyl, in contrast to diphenylmethane, decomposes readily and completely into two molecules of toluene.

Some of the experiments showed that treatment of crude technical products with hydrogen at high temperatures in the presence of alumina-iron oxide catalysts freed them completely from the sulphur compounds which they contained. All experiments were made in an 800-cc. high pressure apparatus. The catalyst was a mixture of iron oxide and alumina, and the weight of the catalyst was 8–10% of the weight of the product being studied. The initial hydrogen pressure was about 70 atmospheres, and the temperature was 440 to 465°.

Alpha-Methylnaphthalene.—Fifty grams of alpha-methylnaphthalene (obtained from the Society for Tar Application, Duisburg-Meiderich) was heated under the conditions mentioned above. The pressure dropped after the apparatus was cooled. In addition to hydrogen, the gases contained 7% of methane. The reaction product was a mass which was part liquid and part crystalline. By cooling and pressing, 27 g. of naphthalene was obtained, which after recrystallization from alcohol melted at 79°. The liquid distilled between 112 and 245°. Benzene hydrocarbons were present in the lower boiling fractions, while the fractions boiling above 200° contained hydronaphthalene, methylhydronaphthalene, and unchanged starting material.

Beta-Methylnaphthalene.—Fifty grams of this substance was heated under the conditions used with the alpha-isomer. Eleven grams of naphthalene was obtained by cooling the liquid and 8 g.

of aromatic hydrocarbons (b.p., 78–200°) distilled over. The remaining liquid was treated with picric acid in alcoholic solution in order to remove unchanged starting material and naphthalene. The picrates were filtered, the alcohol distilled, and the remaining oil was steam distilled; 14 g. of oil boiling at 200–235° resulted. Since the oil no longer formed picrates, it was assumed to contain hydrogenated naphthalene. This product was subjected to dehydrogenation with platinized carbon according to Kaffer.[1] After passing the product 3 times over the catalyst at 310° the dehydrogenated hydrocarbon was cooled to remove naphthalene and finally treated with picric acid. The resulting crystalline product, after six recrystallizations from alcohol, melted at 115°. Titration showed the picric acid content to be 61.63%, whereas 61.72% is required for methylnaphthalene.

Thus, besides dealkylation and the formation of naphthalene, there is also hydrogenation of the original product and splitting of the hydrogenated nucleus into benzene hydrocarbons.

1, 6- and 2, 6-Dimethylnaphthalene.—Hydrogen was absorbed appreciably when heated with these dimethylnaphthalenes for 24 hours. Both hydrocarbons reacted to about the same extent and yielded similar products. Fractionation of 87 g. of the product obtained from 1, 6-dimethylnaphthalene gave the following results: (1) 80–200° (16 g.); (2) 200–230° (43 g.); (3) 230–265° (21 g.).

The first fraction showed d_0^{25}, 0.8653; and n_D^{20}, 1.4890. Sulphonation proceeded smoothly. Oxidation with potassium permanganate produced a large amount of benzoic and phthalic acid which were separated by chloroform.

The second fraction was partly solid at room temperature due to separation of naphthalene. Twenty-eight grams of naphthalene was separated by suction. It melted at 79° after recrystallization and boiled at 216–219°.

The oil remaining after separation of naphthalene was combined with the third fraction and twice distilled over sodium. Dehydrogenation of 18 g. of this oil gave about 5.4 liters of hydrogen and 15 g. of product which formed a picrate melting at 114° after recrystallization from alcohol. Decomposition of this picrate with alkali yielded an oil which solidified to a crystalline mass on cooling. After pressing between filter paper a solid was obtained which melted at about 30°.

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[1] Kaffer, Ber., *57*, 1261 (1924).

Anal. Calcd. for $C_{11}H_{10}$: C, 93.0; H, 7.0. Found: C, 92.7; H, 7.2.

These data indicate success in obtaining the first product of splitting, namely, *beta-methylnaphthalene.*

Products obtained from 2, 6-dimethylnaphthalene were investigated in a similar manner. Quantitative relationships were difficult to establish with these little known hydrogenated alkylnaphthalenes, but the course of the reaction appeared to be analogous for both substances (1, 6- and 2, 6-dimethylnaphthalene).

Paraffin.—Thirty-five grams of white commercial paraffin, (m.p., 52–56°) was converted into liquid by heating 12 hours in the high pressure apparatus in the presence of a catalyst. This liquid (22 cc.) distilled from 50 to 170°; d_0^{25}, 0.7211; n_D^{20}, 1.412. It was similar to light gasoline and reacted neither with sulphuric acid nor with nitrating mixture.

Carbazole.—Experiments proved carbazole to be a most stable substance, a result in complete agreement with the observations of Spilker and Zerbe.[1] On heating 18 hours, carbazole suffered very little change, which consisted principally in the development of the odor of skatol.

Quinoline.—This substance is not very stable. By heating 35 g. of quinoline with hydrogen, a partial splitting of nitrogen in the form of ammonia was observed. The liquid product was steam distilled and bases were neutralized with acid; 7 g. of hydrocarbon separated. This hydrocarbon, distilled over sodium, boiled at 80–150°; d_0^{25}, 0.8763. It reacted very energetically with sulphuric acid and with nitrating mixture.

Diphenylene Oxide.—In contrast to diphenyl and diphenyl ether, diphenylene oxide remained unchanged under the above conditions.

Indene.—Expt. 1: Fifty grams of indene was heated in the presence of a catalyst for 20 hours under 20 atmospheres initial hydrogen pressure. On cooling, a thick, dark liquid was obtained from which only 10 cc. of benzene hydrocarbons could be distilled leaving a tar which could not be distilled without decomposition.

Expt. 2: Fifty grams of indene was heated under 75 atmospheres initial hydrogen pressure. Otherwise the conditions were the same as in Expt. 1. The brownish, mobile liquid was poured off and distilled, giving the following fractions: (1) 90–172° (13 g.);

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[1] Spilker and Zerbe, Zeit. anorg. allgem. Chem., *39*, 1138–1143 (1926).

(2) 172–182° (24 g.); and a small amount of a thick, tar-like substance which remained in the flask.

The first fraction was not further investigated since it evidently consisted of a mixture of benzene hydrocarbons. The second fraction resinified slightly when treated with sulphuric acid after which it was washed with water, dried, and distilled (b.p., 175–176°; d_4^{25}, 0.948).

Anal. Calcd. for C_9H_{10}: C, 92.4; H, 7.6; mol. wt., 119. Found: C, 92.2; H, 7.8; mol. wt., 118.

According to these data, it was concluded that destructive hydrogenation of indene caused hydrogenation of indene to hydrindene followed by a splitting of the product into benzene hydrocarbons.

Tetralin.—Sixty grams of tetralin was heated in the absence of hydrogen and in the presence of a catalyst for 20 hours. After cooling, there was a small residual pressure. The liquid product gave the following fractions: (1) 80–200° (23 g.); (2) 200–225° (19 g.). The fractions solidified due to the presence of naphthalene and a solid mass remained in the flask. Under these conditions, a dehydrogenation of tetralin and a decomposition of the hydrogenated nucleus had taken place.

Dibenzyl.—Fifty grams of dibenzyl was converted into a brownish liquid by heating for 18 hours. This liquid distilled at 108–115°, leaving practically no residue. Its physical properties were: d_4^{25}, 0.8691; n_D^{20}, 1.487. Toluene was the principal product.

Destructive Hydrogenation of Aromatic Compounds under High Hydrogen Pressure [1]

In order to have a better understanding of the cracking of different crude oils in the presence of hydrogen, a study was made under several conditions of the destructive hydrogenation of various individual aromatic and hydroaromatic hydrocarbons which are constituents of certain crude oils. Because of the significance of naphtha and its distillates in the cracking process and considering also that naphtha probably contains perhydroaromatic polycyclic compounds, an investigation was initiated on the destructive hydrogenation of dicycloparaffinic and other hydrocarbons. A study of the above-mentioned reactions of pure substances is important also for an understanding of the thermal decomposition of brown coals. By applying the conditions described above with iron oxide, copper oxide and alumina catalysts, and an initial hydrogen pressure of not less than 70 atmospheres, the destructive hydrogenation of the following perhydrides (completely hydrogenated aromatics) was studied: *Dicyclohexyl, dicyclohexylmethane, 1, 2-dicyclohexylethane,* and *1, 5-dicyclohexylpentane.*

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[1] Ipatieff, Orlow, and Lichatschew, Ber., *63*, 156 (1930).

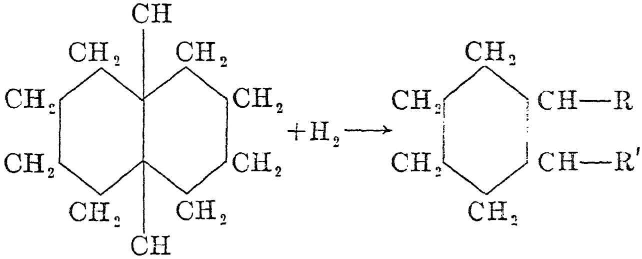
It was to be expected that the splitting of these hydrocarbons would be in accordance with the behavior of the corresponding aromatic hydrocarbons, diphenyl and diphenylmethane, i.e., with the formation of cyclohexane and mono-alkylcyclohexane. Actually, the analogy went even further as shown by the investigation of the decomposition of alpha- and beta-diphenyl paraffins of complex structure, as well as of the previously investigated 1, 4-diphenylbutane and 1, 3-diphenylpropane.

The latter gave homologs of *benzene, toluene,* and *ethyl benzene* whereas cyclohexane homologs also were obtained from dicyclohexylparaffin.

$$C_6H_{11}(CH_2)_aC_6H_{11} + H_2 \rightarrow C_6H_{11}(CH_2)_mCH_3 + C_6H_{11}(CH_2)_nCH_3$$

where $[a = m + n]$

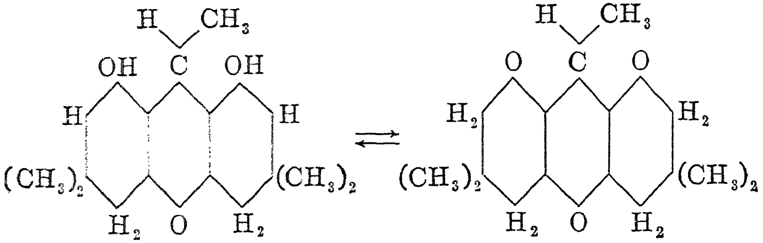
Preliminary experiments on the destructive hydrogenation of decalin yielded a mixture of naphthenes, probably disubstituted derivatives of cyclohexane:



All these reactions took place readily at 440 to 450°. Corresponding to the remarkable stability of carbazole and diphenyloxide (compare preceding experiments) an unusual resistance to splitting was encountered in the hydrocarbon 1, 3, 5-triphenylbenzene. In spite of prolonged heating in the presence of an iron-aluminum catalyst and even with anhydrous ferric chloride no decomposition occurred and not even traces of liquid products were obtained.

The destructive hydrogenation of phenols was investigated by Ipatieff and Petrov and a similar study of this reaction was made by Kling and Florentin on ketones. The study of the destructive hydrogenation of tautomeric keto-phenol compounds was particularly interesting since there is a possibility of the presence of keto-enolic compounds of cyclic character in the high boiling fractions of primary coal tar.

Pentamethyldioxytetrahydroxanthene was chosen for this particular purpose as it is readily obtained.



(I) (II)

Accordingly, primary tar obtained by carbonizing coal at 500° was first freed from asphalt and then subjected to destructive hydrogenation. This tar has not been studied sufficiently, but it should contain compounds closely related to those already studied. By the use of hydrogen under pressure and at a comparatively low temperature, a light gasoline formed from both the light hydrocarbon and the phenols present in the coal tar.

All experiments were made in the high pressure apparatus using definite compounds with a 1:1 mixture of alumina and iron oxide serving as catalyst. The perhydrides were obtained from the corresponding aromatic hydrocarbons by careful hydrogenation in the presence of nickel oxide. In these experiments on destructive hydrogenation the initial pressure of hydrogen was 70–75 atmospheres; the time of heating, 6 hours; the maximum temperature, 440°. The residual gas contained hydrogen and a certain amount of saturated hydrocarbons originating from the removal of side chains or by destruction of the naphthenic ring. In the latter case, the formation of saturated hydrocarbons would take place as shown by the experiment with dicyclohexyl. The liquid from the destructive hydrogenation of dicyclohexyl-paraffins was yellow with a green fluorescence and an odor resembling that of petroleum. When this liquid was distilled, the boiling temperature rose gradually at first and then very suddenly when the unchanged hydrocarbon began to distill. All the data presented in the following table indicate that the products of the reaction contained mixtures of cyclohexane homologs having the formula C_nH_{2n}. Due to insufficient amounts of substances, it was impossible to make a more thorough investigation, or to effect a separation of the components.

TABLE 103

DESTRUCTIVE HYDROGENATION OF DICYCLOHEXYL- AND DIPHENYL-PARAFFINS

STARTING MATERIAL	LIGHT HYDROCARBONS		d_0^{25}	n_D^{26}	ANALYSIS			
					Found		Calculated for C_nH_{2n}	
	Yield, %	B.P., °C.			% C	% H	% C	% H
Dicyclohexylmethane	23	75–105	0.7610	1.4234	85.6	14.4		
Dicyclohexylmethane	23	83–105	0.7644	1.4231	85.9	14.1		
Dicyclohexylethane	45	84–115	0.7843	1.4379	85.7	14.2	85.7	14.3
Dicyclohexylpentane	20	88–150	0.7651	1.4250	85.6	14.4		
Diphenylpropane	65	94–150	0.8675	1.4987	91.7	8.4		
Diphenylbutane	80	107–140	0.8610	1.4963	90.7	9.5		

In the case of diphenyl-substituted paraffins, a break occurred in the paraffinic chain. From diphenylpropane the chief product was methylbenzene mixed with ethylbenzene, and from diphenylbutane the product was ethylbenzene.

1, 3, 5-Triphenylbenzene remained unchanged after heating for 6 hours at 450° in the presence of a mixture of iron oxide and alumina under 75 atmospheres initial hydrogen pressure. Some tar was produced under the conditions described in the presence of ferric chloride, but no liquid product resulted.

Decalin.—When decalin was subjected to destructive hydrogenation, a mixture of hydrocarbons resulted which did not react with sulphuric acid. The main part of the reaction product distilled at 70–150°; d_0^{25}, 0.7688; n_D^{16}, 1.4273.

Anal. Calcd. for C_nH_{2n}: C, 85.7; H, 14.3. Found: C, 85.9; H, 14.3.

Pentamethyldioxytetrahydroxanthene.—Thirty grams of this substance prepared according to the method of Vorlander and Kalpox[1] was heated with a ferric oxide-alumina catalyst for 12 hours under hydrogen pressure at 440°. Considerable coke formed in the bomb and 7 g. of liquid product was obtained which distilled chiefly at 140–300°. Since the odor of this liquid indicated the presence of phenols, it was treated with alkali, with the result that about 25% dissolved. The phenol-free product distilled at the same temperature as before; d_0^{25}, 0.8236.

Anal. Found: C, 89.0; H, 10.8.

Since the hydrocarbon dissolved partially on treatment with sulphuric acid, it probably consisted of a mixture of naphthenes and aromatic hydrocarbons.

Primary Coal Tar.—For use in these experiments a primary tar was separated from water and mineral matter by dissolving it in xylene, filtering the solution, and distilling to 160° to remove the xylene. Its phenol content was about 40%. The tar thus obtained was treated four times at 40–70° with light gasoline which did not dissolve asphalts. The asphalt content of the tar was so determined as 27%. After removing the gasoline by distilling up to 160°, the tar appeared as a thick, dark oil.

Five hundred and fifty grams of this tar was catalytically hydrogenated at 430° in a rotating 2.5-l. autoclave under an initial hydrogen pressure of 95 atmospheres. On cooling at the end of the reaction, the pressure was 70 atmospheres and the residual gas contained 7% of methane. From the liquid products, 28% gasoline and 3.2% water were distilled, up to 150°. The formation of water during the reaction indicates that phenols

TABLE 104

PROPERTIES OF GASOLINE FORMED BY DESTRUCTIVE HYDROGENATION OF PRIMARY COAL TAR

BOILING RANGE, °C.	% OVER	n_D^{18}	d_0^{24}
Up to 55	5.5	1.3732	0.6368
55– 75	11.0	1.3767	0.6579
75– 95	27.0	1.3951	0.6979
95–115	33.5	1.4135	0.7345
115–135	13.0	1.4272	0.7594
135–150	10.0	1.4393	0.7793

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[1] Vorlander and Kalpox, Ann., *307*, 373 (1899).

also took part in the benzene formation. The gasoline was redistilled, then washed with diluted sulphuric acid, alkali, and water.

Treatment of the gasoline (p. 412) with 20% by volume of fuming sulphuric acid showed the presence of 3% of benzene hydrocarbons.

Conclusions

The experiments described above give an approximate idea as to the fate of the various constituents of coal tar during destructive hydrogenation. These preliminary experiments have already indicated the possibility of a partial explanation as to the origin of the different products in a particular reaction. It is intended to study the reactions occurring in destructive hydrogenation in greater detail, as they are very important technically. This problem has been studied also by many other investigators including Spilker and Zerbe, and Kling and Florentin.[1]

CRACKING OF KETONES UNDER PRESSURE[2]

Study of the condensation of acetone (refer to chapter on condensation) under pressure at 350–400°, indicated that increase in temperature, up to 500°, would cause the decomposition to proceed parallel with condensation and result in the separation of carbon and formation of gases containing appreciable quantities of carbon monoxide. It has been stated that the carbon content of the condensate increases with increase in temperature and for this reason it was interesting to study the cracking of acetone under pressure in the presence of alumina as catalyst at 500° and higher. Apparently this reaction is still more interesting because previously the decomposition of ketones was investigated only at ordinary pressure and high temperature (1000°) in the absence of an added catalyst. However, it is doubtful whether all the products obtained at this high temperature were primary products of the decomposition of acetone or whether they were secondary products formed from the primary.

It is known that Barbier and Roux[3] obtained acetophenone, benzophenone, and a trace of naphthalene when acetone was led through a copper tube at 1000°. The accompanying gaseous products consisted mainly of carbon monoxide, methane, hydrogen, and ethylene. Only an insignificant amount of liquid condensate was formed in which the presence of naphthalene was proved. Besides giving a large amount of carbon, the decomposition of benzophenone produced benzene, diphenyl, p-diphenylbenzene, and a small amount of benzaldehyde. The gaseous products were carbon monoxide and hydrogen. Acetophenone gave the same products as benzophenone and also a small amount of toluene.

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[1] Kling and Florentin, Bull. soc. chim., (4), *41*, 864 (1927).

[2] Ipatieff and Petrov, Ber., *60*, 1956 (1927).

[3] Barbier and Roux, Bull. soc. chim., (2), *46*, 268 (1886).

These investigators used the following equations in explaining the origin of diphenyl and p-diphenylbenzene from benzophenone:

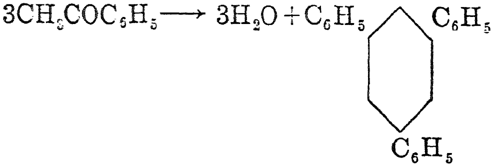
$$2(C_6H_5)_2CO \rightarrow 2CO + C_6H_6 + C_6H_4(C_6H_5)_2$$

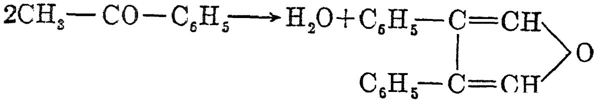
$$(C_6H_5)_2CO \rightarrow CO + C_6H_5C_6H_5$$

They ascribed the formation of these products to the direct decomposition of the ketones.

Investigations on the decomposition of ketones at a temperature not exceeding 550°, under pressure, and in the presence of alumina gave the following results:

When acetophenone was heated at 290–300°, 50% of the ketone underwent a change resulting in a 30% yield (calculated on the amount of ketone used) of products consisting of a mixture of triphenylbenzene, 3, 4-diphenyl furane, and a red tar-like residue, part of which could be distilled. Apparently, these products originated according to the following equations:





The formation of these products by heating acetophenone with zinc chloride in a sealed tube was described by Engler and Dengler,[1] but our experiments were different in that the acetophenone was heated in an iron tube and the yield of diphenyl furane was considerably higher.

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[1] Engler and Dengler, Ber., *26*, 1445 (1893).

At 380–420°, all of the acetophenone entered into the reaction, producing a 15% yield of a mixture of benzene, toluene, ethylbenzene, and o-xylene. The residue was a tar containing no traces of diphenyl or p-diphenylbenzene, substances found in a similar residue by Barbier and Roux. Only insignificant amounts of benzoic acid were found.

Assuming that ethylbenzene might be the product of the hydrogenation of acetophenone by means of hydrogen originating during the reaction in the presence of iron,[1] experiments were made in which acetophenone was heated with hydrogen at 380–420°. Forty per cent of the acetophenone was converted into a mixture of benzene, toluene, ethylbenzene, and o-xylene; no benzoic acid was formed.

The primary products obtained by the cracking of acetophenone were benzene and toluene; ethylbenzene was a product of reduction. The formation of o-xylene might be due to the decomposition of acetophenone according to the equation:

$$2CH_3COC_6H_5 \rightarrow C_6H_4(CH_3)_2 + C_6H_6 + CO$$

or by isomerization of ethylbenzene. It is intended to return to the question of the possibility of isomerizing the alkyl benzenes under our experimental conditions.

No dehydration reaction occurred on heating benzophenone, and even after heating to 430° this substance still remained unchanged. Complete decomposition of benzophenone occurred on heating at 500–550°. Carbon and gas were the main products together with approximately a 12% yield of liquid from which benzene and diphenylmethane were separated. Neither diphenyl nor p-diphenylbenzene was found.

An 80% yield of diphenylmethane was obtained by heating benzophenone at 400–430° in an iron tube with hydrogen in the presence of alumina. Only 20% of the benzophenone decomposed into benzene and tar. Therefore, hydrogenation of benzophenone in an iron tube under pressure in the presence of alumina is a good method of preparing diphenylmethane. The results obtained permit the following conclusions.

The theoretical equations presented by Barbier and Roux concerning the decomposition of acetone with the accompanying formation of diphenyl and para-diphenylbenzene do not correspond with the facts. These substances are not primary products of the decomposition of acetone, but may originate from the benzene, toluene, and other decomposition products of the ketone, although only at high temperatures. When the ketone was heated under pressure in an iron tube, decomposition was accompanied by reduction of the ketonic group with the formation of the corresponding hydrocarbon. When the ketone was heated in an iron tube in the presence of aluminum oxide, the yield of hydrocarbon increased (almost the theoretical yield for benzophenone), the yield depending upon the stability of the ketone.

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[1] Ipatieff, "Catalytic Action of Iron," Ber., *40*, 1270 (1927).

On heating acetone at 500–530° the production of a large amount of saturated hydrocarbons, propane for example, indicated that these decomposition reactions were analogous to those discussed for acetophenone and benzophenone. Forty per cent of the liquid condensate consisted of an aqueous layer having an odor similar to that of phenol. This substance, separated by means of sodium hydroxide, distilled between 200 and 230°. Based upon the original amount of acetone, a yield of 1–2% of phenol was obtained. The remaining 60% of the liquid condensate consisted of hydrocarbons which distilled at 70–340° with the main fraction at 150–180°. In order to explain the origin of phenol from acetone, the fractions boiling at 200–220° and 220–280°, obtained by condensation of acetone at 350–400°, were heated at 500–530°. (Refer to chapter on condensation.) These fractions contained the unsaturated cyclic ketones, isophorone and xylitone. Fifty per cent of the fractions decomposed with formation of carbon and gas. The yield of phenols was greater in this case, totaling 10–15% for the fraction boiling at 200–220°, which consisted chiefly of isophorone. An experiment with isophorone, which was prepared according to Freund and Speyer [1] by the action of sodamide upon acetone, gave a phenol yield of approximately 20%.

The liquid condensate, insoluble in sodium hydroxide, distilled at 70–340°, and the chief fraction, which boiled at 150–180°, consisted of *cumene*, *pseudo-cumene*, and *mesitylene*. Closer investigation of the phenolic fraction showed that it consisted almost exclusively of *1, 3, 5-xylenol.*

The formation of phenol from isophorone might be explained by the isomerization of the ketonic form into the enolic form due to the removal of methane and the formation of a double bond in the ring.

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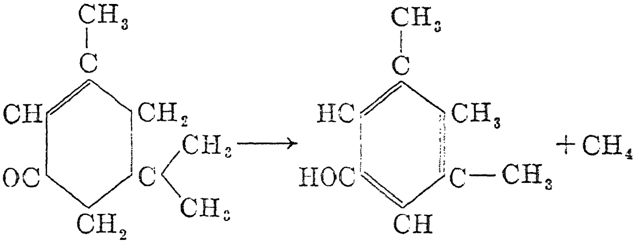
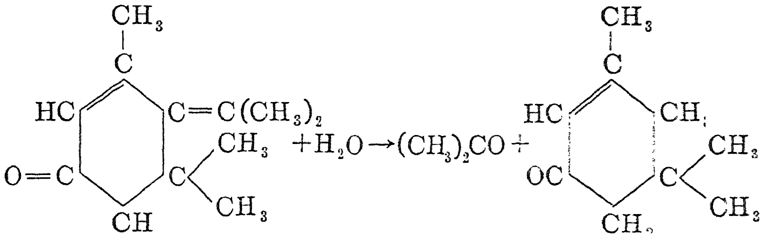
[1] Freund and Speyer, Ber., *35*, 2332 (1902).



Xylitone,[1] obtained from the fraction boiling at 220–280°, was converted primarily into isophorone, and the latter gave xylenol.



The preparation of 1, 3, 5-xylenol in the laboratory under or, dinary conditions has been a very difficult problem in the past-but now it is believed that our method gives the best yields and in a comparatively short time. The transformation of a cyclic ketone into a phenol by pyrolysis has not yet been fully explained, but a certain analogy might be drawn between this reaction and the dehydrogenation of ketones. Because of their technical interest such transformations should be investigated. Extraction of coal tar with liquid sulphur dioxide and benzene, as well as distillation in vacuum, proved the absence of aromatic compounds, especially phenols,[2] and showed the presence of naphthenic alcohols, ethers, and acids.

Furthermore, an investigation of the components distilling at low temperatures indicated the presence of acetone and other ketones.[3] From these facts it is concluded that the phenols of coal tar are formed by the cracking of various cyclic ketones and that it is possible for these ketones to originate by dehydrogenation of the corresponding cyclic alcohols, as well as from acids or ethers.

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[1] The structure of xylitone has not been definitely established.

[2] Pictet, Ber., *44*, 2488 (1911); Bone, Proceed. Roy. Soc. London, A, *96*, 119 (1920); A, *105*, 608 (1929); Tropsch, Brennst. Chemie, *3*, 177 (1926).

[3] Schütz, Ber., *56*, 162 (1923).

If a comparison be made of the results obtained by the condensation and decomposition of acetone in the presence of aluminum oxide under pressure, the possibility of the occurrence of the following reactions should be recognized: formation of mesityl oxide, isophorone, xylitone, and mesitylene at 350–400°, at which temperature both reversible and irreversible (the formation of mesitylene) reactions take place. Increasing the temperature to 500–550° changes the course of the reactions from reversible to irreversible and causes a maximum liberation of water with the formation of unsaturated cyclic ketones (isophorone and xylitone). With complete elimination of water a mixture of aromatic hydrocarbons, chiefly mesitylene, is obtained. Partial reaction accompanied by the separation of methane leads to the formation of symmetrical 1, 3, 5-xylenol.

Experiments were carried out in the high pressure apparatus by heating various ketones with 1% by weight of aluminum hydroxide.

Acetophenone.—This ketone was heated at a maximum temperature of 270–300° for 12 hours during which time small amounts of hydrogen and a somewhat resinous liquid were formed. The latter was dried with sodium sulphate and distilled under diminished pressure. About half of the acetophenone treated was recovered unchanged on distillation. The residue was subjected to repeated crystallization which resulted in the separation of two compounds, one melting at 109° and readily soluble in alcohol, the other melting at 169° and sparingly soluble in alcohol.

The first product was 3, 4-diphenylfurane.

Anal. Calcd. for $C_{15}H_{12}O$: C, 86.6; H, 5.7. Found: C, 87.5; H, 5.7.

The second product was 1, 3, 5-triphenylbenzene, $C_{24}H_{18}$, which gave the following analytical data.

Anal. Calcd. for $C_{24}H_{18}$: C, 94.1; H, 5.9. Found: C, 93.7; H, 6.0.

In another experiment acetophenone was heated at 380–420° for 20 hours at a maximum pressure of 75 atmospheres; after cooling, the pressure was 20 atmospheres. Analysis of the gas gave the following figures: CO_2, 3.8%; CO, 64%; C_nH_{2n}, 1.2%; C_nH_{2n+2}, 2.5%; H_2, 9.2%.

A very resinous liquid was obtained with an odor resembling that of an aromatic hydrocarbon. This was distilled with steam. From 180 g. of acetophenone, 28 g. of a liquid was obtained which distilled at 80–200°. Distillation through a column gave the following fractions: (1) 80–125° (9 g.); (2) 125–140° (7 g.); (3) 140–150° (9 g.); (4) 159–200° (3 g.).

In the first fraction, benzene was determined according to the method of Hoffman and Arnoldi[1] by means of nickel cyanide. After removal of benzene, toluene was identified by converting it into dinitrotoluene melting at 71°. The presence of ethylbenzene in the fraction boiling at 125–140° was shown by means of the method of Friedel and Crafts[2] by preparation of a bromide melting at 141.5°, as well as by oxidation by dilute nitric acid to benzoic acid. The fraction boiling at 140–150°, which according to analysis was a mixture of hydrocarbons of the formula C_8H_{10}, nitrated to liquid nitro products only, and when subjected to prolonged oxidation with dilute nitric acid according to Piccard[3] gave a mixture of benzoic and o-phthalic acids. After removing the benzoic acid with chloroform, the o-phthalic acid was identified by the formation of fluorescein. The third fraction contained a mixture of ethylbenzene and o-xylene; the fourth fraction, traces of unchanged acetophenone. Only a small amount of benzoic acid could be recovered from the tar.

In the third experiment, 70 g. of acetophenone was heated with hydrogen (initial pressure, 50 atmospheres). The temperature was 380–420°; duration of heating, 18 hours; maximum pressure, 125 atmospheres. Less tar was formed than in the second experiment. Twenty-six grams of aromatic hydrocarbons (b.p., 80–200°) was distilled over with steam. Investigation of this distillate showed the presence of benzene, toluene, ethylbenzene, and o-xylene with a yield (about 20%) of ethylbenzene higher than in the preceding experiment.

Benzophenone.—One hundred and fifty grams of benzophenone was used in the experiment at 500–550° under a maximum pressure of 50 atmospheres. The pressure after cooling was 12 atmospheres and the gas remaining in the bomb consisted of CO_2, 37.3%; CO, 2.7%; H_2, 33.3%; C_nH_{2n+2}, 26.7%. About 20 g. of a liquid was formed with an aromatic odor resembling that of oranges; the residue was carbon. In this case the main course of the reaction was as follows:

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[1] Hoffmann and Arnoldi, Ber., *39*, 339 (1906).

[2] Friedel and Crafts, Compt. rend., *101*, 1218 (1885).

[3] Piccard, Ber., *12*, 579 (1879).

$$(C_6H_5)_2CO \rightarrow 5H_2 + 12C + CO$$

The theoretical amount of carbon monoxide was 16.6%; that of hydrogen, 83.4%. The gas analysis figures obtained by us show that we were dealing here with another type of decomposition and hydrogenation of carbon monoxide, according to the following equations:

$$2CO \rightarrow CO_2 + C$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

and that in all probability there were other reactions taking place.

The liquid distilled between 80 and 350° and gave fractions at 90–90° and 250–270°. In the first fraction the presence of benzene was shown according to the method of Hoffmann and Arnoldi. From the second fraction, the portion distilling at 260–263° was analyzed.

Anal. Calcd. for $C_{13}H_{12}$: C, 92.8; H, 7.3. Found: C, 92.6; H, 7.3.

Therefore, the products resulting from the cracking of benzophenone were benzene and diphenylmethane. At 380–420° (18 hours) and 440–470° (8 hours) the benzophenone did not undergo any change.

By heating 70 g. of benzophenone with hydrogen (pumped in at 60 atmospheres) at 400–430° for 20 hours, a maximum pressure of 125 atmospheres was reached; after cooling, the pressure was 35 atmospheres and from the bomb was obtained 60 g. of liquid having an odor similar to that of diphenylmethane. From this liquid were obtained 2 g. of benzene and 52 g. of a white crystalline mass identified as diphenylmethane.

Acetone.—By heating 400 cc. of acetone at a maximum temperature of 500–550° for 24 hours, large amounts of gases were obtained. Analysis of these gases gave the following data: CO_2, 11.25%; CO, 7.5%; C_nH_{2n+2}, 63.5%; H_2, 17.5%. Two hundred cc. of a liquid was obtained, 40% of which consisted of an aqueous layer. Half of the acetone decomposed into carbon and gas. The condensate was washed with water and shaken with sodium hydroxide and then with sulphuric acid, thereby reducing its volume to

100 cc. The phenols were dried with sodium sulphate and distilled. They boiled at 200–230°, remained liquid at room temperature, and gave a red coloration with Millon's reagent and a blue-green coloration with ferric chloride. That portion of the condensate which was insoluble in sodium hydroxide was distilled; the boiling range was 70–340°, the main portion distilling at 150–180°.

One hundred and twenty grams of the condensation product of acetone (b.p., 220–280°) obtained by heating acetone at 350–400° was subjected to a second cracking at 500–550° for 14 hours; 60 g. of liquid was obtained from which 6 g. of phenols was isolated. The portion of the condensate which was insoluble in alkali distilled at 70–340°; the main fraction at 150–180°.

Isophorone.—Ninety-five grams of isophorone, prepared according to the method of Freund and distilling at 90–116° at 16 mm., was heated at 500–550° for 4 hours; 14 g. of phenols boiling at 200–230° was obtained.

The phenol fractions obtained from acetone were combined with the phenols from isophorone since they were identical. Distillation of 20 g. of these phenols yielded the following fractions: (1) 200–210° (6 g.); (2) 210–225° (12 g.). Only the first fraction gave a color reaction with ferric chloride. On nitration, according to Raschig, only traces of nitro compounds were obtained, but on bromination both fractions gave good yields of a bromide melting at 162°. Analysis of both fractions gave data approximating the formula of xylenol.

Fraction boiling at 200–210°.

Anal. Calcd. for C_7H_8O: C, 77.7; H, 7.4. Found: C, 77.9; H, 8.1.

Fraction boiling at 210–225°.

Anal. Calcd. for $C_8H_{10}O$: C, 78.6; H, 8.2. Found: C, 78.2; H, 8.2.

The bromine content, determined according to the method of Carius, was found to be 66.4%; $C_8H_7OBr_3$ requires 66.9% of bromine. Therefore, the data indicate that these fractions consisted chiefly of *1, 3, 5-xylenol.*

The hydrocarbons obtained by the cracking of acetone were not separated by fractionation, but the chief fraction, boiling at 150–180°, was investigated.

Anal. Calcd. for C_9H_{12}: C, 89.9; H, 10.1. Found: C, 89.9; H, 10.4; d_0^{25}, 0.8552; n_D^{17}, 1.4942.

The trinitro derivative obtained from this fraction, prepared according to Fittig, melted over a wide range, 169–227°; the bromine derivative melted at 222–224°.

Anal. Calcd. for $C_6H_9Br_2$: Br, 67.22. Found: Br, 67.27.

Thus, by the action of high temperature, pressure, and aluminum oxide upon isophorone and xylitone, the main product was a mixture of aromatic hydrocarbons of the composition C_9H_{12}, in which mesitylene predominated.

It is interesting to note that by distilling isophorone with phosphorus pentoxide, the resulting hydrocarbon fraction, as shown by Kerp,[1] contained only cumene and pseudocumene, since the melting point of the nitro derivatives was between 137–157° and that of the bromine derivatives 228–231°.

Catalytic Cracking of Cyclic Ketones [2]

In the present work it was intended to study the cracking of homo-isophorone (the analog of isophorone, formed by the condensation of methylethyl ketone) and of saturated cyclic ketones, as well as other cyclic ketones containing a double bond in the side chain. Homo-isophorone, 1-methylcyclohexanone-2, and pulegone were heated in a high pressure apparatus in the presence of iron oxide. Phenols were obtained from homo-isophorone and pulegone. Methylcyclohexanone experienced the usual decomposition of cyclic ketones with the formation of hydrocarbons and the removal of carbon monoxide; the formation of phenols was not observed. These results confirmed our mechanism of the formation of phenols from ketones which assumes that their formation must be preceded by an intermediate transition through the tautomeric enolic form. In order to make possible the formation of phenol, it is necessary that the cyclic ketone contain a double bond. As shown by experiments carried out with pulegone, a double bond may also be present outside of the ring. In the latter case, no doubt the double bond is shifted into the ring, and under the influence of heating and a catalyst, an isomeric conversion of the ketone occurs.

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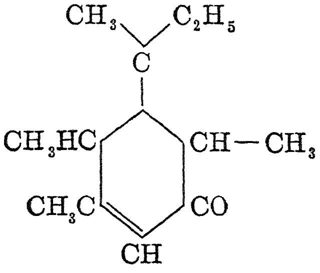
[1] Kerp, Ann., *290*, 123 (1896).

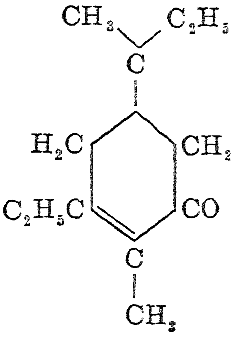
Trinitrozates,	melting	point	109°
Trinitropseudocumol,	"	"	185°
Trinitromesitylene,	"	"	224°
Tribrompseudocumol,	"	"	225–233°

[2] Ipatieff and Petrov, Ber., *60*, 2545 (1927).

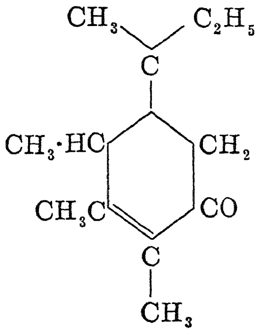
Homo-Isophorone.—In contrast to isophorone, homo-isophorone obtained by the condensation of methylethyl ketone by means of sodamide may contain theoretically not only one isomer, but four (alpha, beta, gamma, and delta), which cannot be separated by distillation.



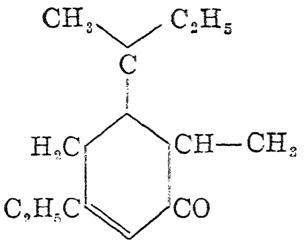
(alpha)



(beta)



(gamma)



(delta)

In heating homo-isophorone (a mixture of isomers), it was desired to ascertain the following: (1) whether cracking of the analog of isophorone gives the same type of decomposition as isophorone; (2) which of the two groups located in position 1, the methyl or the ethyl, splits off with the formation of a new double bond.

The experiment gave an affirmative answer to the first question. Regarding the second question, the low boiling point of the phenol mixture which was obtained, as well as the data from the analysis, led to the conclusions that not only the ethyl group present in the first position splits off, but the other ethyl group attached to another carbon atom is also removed. The yield of hydrocarbons in this case was very small. In making a comparison of the cracking of homo-isophorone with that of isophorone, it can be concluded that the stability of the former is less with the result that its decomposition gives a smaller yield of hydrocarbons.

Ninety grams of homo-isophorone (fraction boiling at 129–133° at 15 mm. pressure) was heated for 2 hours in the high pressure apparatus at 470–486° in the presence of ferric oxide. Considerable gas and carbon were formed. The resulting gas had the following composition: CO_2, 5.66%; CO, 4.1%; H_2, 4.4%; C_nH_{2n+2}, 86.6%. Fourteen grams of phenols boiling at 210–225° and 5 g. of hydrocarbons boiling at 60–240° were obtained. Analysis of the phenol fraction gave figures corresponding closely to the formula for xylenol.

Anal. Calcd. for $C_8H_{10}O$: C, 78.6; H, 8.2. Found: C, 78.2; H, 8.6.

The bromide of this phenol melted at 135–150°, thus differing from the bromide of isophorone. This fact indicated that the phenolic fraction consisted of a mixture of phenols, as would be expected.

1-Methylcyclohexanone-2.—The 1-methyl-cyclohexanone-2 was prepared from 1-methylcyclohexanol-2. It boiled at 162–163° and gave a semi-carbazide melting at 191°.

1-Methylcyclohexanone-2 underwent decomposition when heated at 470–490° in an iron tube under pressure. There was no formation of phenols and the liquid product consisted only of hydrocarbons which were similar in their properties to the decomposition products of cyclohexane. A noticeable characteristic of the decomposition of saturated cyclic ketones was the formation of negligible amounts of toluene. Also, formation of a very small amount of high boiling products was noted. There were probably condensation products which were not investigated thoroughly.

Seventy grams of 1-methylcyclohexanone-2 and 3 g. of iron filings were heated at 470–490° for 2 hours. The maximum pressure was 125 atmospheres. A dark colored liquid was formed, as well as carbon and gas. Gas analysis gave the following data: CO_2, 13.4%; CO, 17%; H_2, 4.2%; C_nH_{2n+2}, 66%.

The liquid product, on distillation, yielded 22 g. of a mobile, slightly yellowish liquid distilling at 40–200° and having an odor similar to that of amylene. The rest of the liquid distilled with decomposition in the presence of air and formed tar. Not even traces of phenols were found. The experiment repeated in the presence of iron oxide gave identical results.

About 70 g. of a liquid distilling at 40–200° was repeatedly distilled through a column, but it was impossible to fractionate the liquid into its components. Treatment with sulphuric acid showed that the product contained about 40% of unsaturated compounds. The liquid insoluble in sulphuric acid was again distilled and analysis of the various fractions led to the conclusion that they consisted of a mixture of various hydrocarbons containing slight amounts of aromatics, namely, toluene.

TABLE 105

Fraction No.	B.P., ° C.	n_D^{18}	d_{25}^{25}	% C	% H
1	60– 85	1.4080	0.7294	86.1	14.2
2	85–100	1.4291			
3	100–120	1.4378	0.7862	86.6	12.9
4	120–150	1.4530			
5	150–200	1.4631	0.8308	87.2	12.6

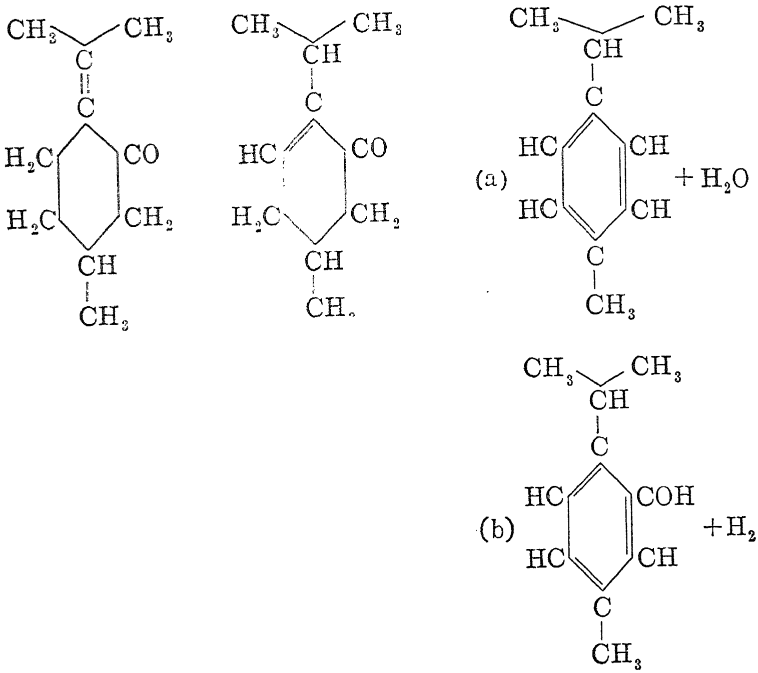
The formula C_nH_{2n} requires C, 85.7%; H, 14.3%. Nitration of the third fraction gave only a small amount of dinitrotoluene.

Pulegone.—Pulegone was decomposed when heated in an iron tube in the high pressure apparatus at the comparatively low temperature of 380–400°. Among the reaction products were found phenols boiling between 196 and 220°, but there was no thymol, cyclic or unsaturated hydrocarbons, or cymol. The origin of cymol may be considered analogous to the formation of mesitylene in the decomposition of isophorone as previously stated. For pulegone the principal course of the decomposition may be represented as is shown on p. 426.

Absence of thymol in the reaction products was the result of the action of high temperature upon this phenol. When thymol was heated at 400°, it was converted into a complex mixture of phenols, half of which distilled at 200–220°.

The third type of decomposition of ketones, the splitting of the carbonyl group, which is the chief reaction in the cracking of methylcyclohexanone, occurred only to a very slight extent with pulegone and with isophorone.

Seventy grams of pulegone (from Kahlbaum) was heated at 380–400° for 1.5 hours under a maximum pressure of 50 atmospheres. Fifty grams of a highly resinous liquid was obtained, 22 g. of



which distilled at 40–230°, leaving resinous bottoms. Of the 22 g. of distillate, 15 g. consisted of hydrocarbons and 7 g. of phenols. Gas analysis gave the following data: CO_2, 7.5%; CO, 22%; C_nH_{2n+2}, 71%.

The phenolic fraction distilled at 196–200° and the van Italie reaction [1] indicated the absence of thymol. A special experiment with thymol in the presence of ferric oxide, showed that thymol is converted into a mixture of low boiling phenols under these conditions. The hydrocarbons obtained from pulegone contained 30% of unsaturated hydrocarbons. The hydrocarbons insoluble in sulphuric acid were separated by distillation into the following fractions: (1) 70–100°; (2) 100–120°; (3) 120–150°; (4) 150–180°. Investigation of the first three fractions showed that they were completely analogous to the corresponding fractions obtained from methylhexanone, that is, they consisted chiefly of saturated cyclic compounds. Investigation of the fourth fraction indicated that it consisted principally of cymene; n_D^{18}, 1.4768.

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[1] van Italie reaction, Arch. Pharm., *27*, 228.

Anal. Calcd. for $C_{10}H_{14}$: C, 89.5; H, 10.5. Found: C, 88.0; H, 11.5.

Bromination, according to Gustavson, gave pentabromtoluene melting at 282°.

Anal. Calcd. for $C_7H_3Br_5$: Br, 82.1. Found (Carius): Br, 82.5.

CRACKING OF ACETONE UNDER PRESSURE IN THE PRESENCE OF ZINC CHLORIDE [1]

In a series of investigations by Ipatieff and Petrov, the condensation of acetone at high temperatures and pressures in the presence of various catalysts, particularly zinc chloride, was investigated.

It is to be noted that zinc chloride gives a large yield of hydrocarbons, but at relatively low temperatures. Besides mesitylene there was formed also a considerable amount of other hydrocarbons which have not yet been thoroughly studied. Having in view a more detailed study of the primary products of the cracking of acetone, an investigation was made of the cracking of acetone in the presence of zinc chloride under pressure at 300–320° in order to obtain a large amount of the liquid product. Under these conditions, as may be seen also from preceding work, mesityl oxide, isophorone, and xylitone were formed in addition to hydrocarbons. These ketones were also subjected to cracking, with the resultant formation of hydrocarbons, a mixture being obtained which distilled from 40 to 340°. After repeated distillation over metallic sodium, the hydrocarbons were separated from the compounds containing oxygen. The content of unsaturated hydrocarbons was determined by the iodine number as well as by treatment with 80 to 100% sulphuric acid. The presence of aromatic compounds was determined by means of nitrating mixture and by treatment with fuming sulphuric acid.

Thus, it was established that the principal product was unsaturated hydrocarbons and mesitylene, naphthenes being found in only negligible amounts. The absence of naphthenes was demonstrated not only by analysis, but also by hydrogenation. The unsaturated hydrocarbons in the lower boiling fraction of the cracking products belonged to the olefin series; those of the kerosene fraction were polymerization products of diolefins. By the action of high temperature upon the latter, secondary products could be obtained.

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[1] Ipatieff, Ivanow, and Petrov, Ber., *63*, 2806 (1930).

An attempt was made to separate unsaturated hydrocarbons by treatment with mercuric acetate. In the application of this method, reference was made to the work of Tropsch [1] who used mercuric acetate in separating unsaturated hydrocarbons from an artificial benzine mixture which he obtained by synthesis from water gas at ordinary pressure. However, separation of unsaturated hydrocarbons by this method was unsuccessful. The low boiling hydrocarbons of our mixture gave mercuric compounds which were volatile with steam and underwent partial decomposition on steam distillation. Further, it is to be noted that these low boiling hydrocarbons were partially oxidized by the mercuric salts; and also that high boiling terpene hydrocarbons reacted slowly with mercuric acetate with simultaneous oxidation. According to data obtained from the literature, not all unsaturated hydrocarbons give normal mercuric compounds; some of them do not give mercuric compounds at all, and some are oxidized.

As to which hydrocarbons do not give mercuric compounds and which hydrocarbons oxidize, the data in the literature are contradictory. Thus, for example, the terpenes of the alkyl series, according to Balbioni and Paolini,[2] give mercuric compounds, whereas hydrocarbons of the propenyl series are oxidized to the corresponding alcohols. According to Tauss,[3] pinene forms normal mercuric compounds, as well as dipentene, limonene, and other terpene hydrocarbons. Previously, it had been assumed that at least a part of the terpenes found in the mixture were formed by the polymerization of isoprene. They belong to the type of dipentenes containing the allyl and propenyl groups, and it is plausible to assume that by distillation over sodium two propenyl groups are formed. According to Balbioni, the oxidation of terpenes under our conditions is evidence of their propenyl character.

No mercuric compounds are formed by the low boiling olefins of gasoline fractions. It is also known that olefins of isostructure and those with many side chains such as, for example, tetramethylethylene, trimethylisobutylethylene, diamylene, and others, as distinguished from olefins of normal structure, do not give mercuric compounds.

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[1] Tropsch, Brennst. Chemie, *10*, 337 (1929).

[2] Balbioni and Paolini, Chem. Cent., *25*, 932 (1900); Balbioni, Ber., *35*, 2994 (1902); *36*, 3578 (1903).

[3] Tauss, Petroleum, *13*, 649 (1918); C. 1909, II, 125; Chem. Cent., *37*, 1023 (1913).

In the lower boiling gasoline fraction, hydrocarbons of the isostructure predominate. The isostructure of hydrocarbons originating under the present type of operation was confirmed by Ipatieff's investigations [1] on the specific action of zinc chloride at ordinary pressure. Secondary butyl alcohol when passed over alumina gave n-butylene and traces of isobutylene, whereas when passed over zinc chloride it gave large amounts of isobutylene. Furthermore, it should be mentioned that isopropylethylene was isomerized into trimethylethylene when passed over alumina. The antiknock action of cracked benzines might be explained by the presence of considerable amounts of olefins of isostructure; zinc chloride is to be considered as a specific example of a catalyst suitable for increasing the isoolefin content of such products. An accurate study of the formation of synthetic benzine by the cracking of various materials in the presence of zinc chloride and other specific catalysts deserves careful consideration from both qualitative and quantitative viewpoints.

In the cracking of acetone, the following procedure was followed: Two hundred and fifty cc. of acetone and 15–20 g. of zinc chloride were used in each experiment. The time of heating was 6 hours; maximum temperature, 300–320°; pressure at the end of the reaction, 25–30 atmospheres.

The analytical data on the exit gas are not presented here as they have been tabulated elsewhere. The condensate collected from a number of experiments amounted to 6 liters, but after washing with water its volume decreased 50%. The resulting product, after drying with calcium chloride, was distilled into the following fractions: (1) 35–200° (77%); (2) 95–180° (23%, 27 mm.). In order to separate oxygen-containing compounds, both fractions were heated with metallic sodium until analysis gave a carbon-hydrogen total of 100%. After this treatment with sodium, the first fraction distilled at 40–180° at ordinary pressure, the second at 70–180° at 14 mm. Analysis of the fractions gave the following data:

Fraction boiling at 40–180°: C, 88.0%; H, 12.2%.
Fraction boiling at 70–180° (14 mm.): C, 88.5%; H, 12.0%.

After distillation over sodium, the total amount of the condensate was 1419 g., 78% of which was in the first fraction, 22% in the second. In order to determine the content of unsaturated hydrocarbons in the two fractions, the iodine number was determined, and also the percentage of olefins soluble in 80% sulphuric acid (method of Egloff and Morrell).[1]

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[1] Ipatieff, Ber., *40*, 1827 (1907).

The first fraction (b.p., 40–180°) had an iodine number of 85 and 18.3% dissolved in 80% sulphuric acid. The second fraction (b.p., 70–180°) had an iodine number of 53 and 15.2% dissolved in 80% sulphuric acid. Further treatment of an individual sample with 100% sulphuric acid (3.5 volumes and shaking for half an hour) removed both the unsaturated and the aromatic hydrocarbons.

The first fraction (b.p., 40–180°) contained a total of 80.8% of unsaturated and aromatic hydrocarbons. The second fraction (b.p., 70–180° [14 mm.]) contained a total of 85.0% of saturated and aromatic hydrocarbons. Therefore, 19.2% of the first fraction consisted of naphthenic and paraffinic hydrocarbons and 15% of the second fraction.

An attempt was made to isolate the unsaturated hydrocarbons by means of mercuric acetate. For this purpose, the first fraction was shaken with mercuric acetate in a ratio of 1:9 for 3 hours at room temperature. The precipitate was separated from the liquid, and the absorbed saturated hydrocarbons removed therefrom with steam. In order to separate saturated hydrocarbons from oxidation products, this part of the fraction was distilled over metallic sodium. The precipitate was filtered, steamed, decomposed with hydrochloric acid, and the product steam distilled. Three hundred grams of precipitate obtained from the first fraction gave 25 g. of hydrocarbon which was treated as described above. The iodine number was found to be 44 for the saturated and 54 for the unsaturated part. The iodine number of the whole fraction, previous to treatment with mercuric acetate, was 85. Experiment, therefore, showed that separation of a mixture of unsaturated and saturated hydrocarbons by means of mercuric acetate is not feasible. A similar result was obtained with a saturated solution of mercuric acetate in methyl alcohol, with this difference that the precipitate of mercuric acetate settled out only after 5 days. The second fraction was treated in the same way, but it did not give positive results.

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[1] Egloff and Morrell, Ind. Eng. Chem., *18*, 354 (1926).

After an unsuccessful attempt to separate the unsaturated hydrocarbons by mercuric acetate, both fractions were combined and the unsaturated hydrocarbons were removed by 80% sulphuric acid. The residual hydrocarbon (130 g.) was distilled into the following fractions: (1) 70–90°; (2) 90–120°; (3) 120–152°; (4) 152–200°. The first three fractions comprised 15% of the total amount of hydrocarbons; the fourth fraction, 85%.

According to the method of Hoffmann and Arnoldi, it was shown that the first fraction contained only traces of benzene, and according to the results of nitration, the second fraction contained only traces of aromatic hydrocarbons. The third fraction did not give any definite nitro compound. The fourth fraction was divided by distillation into a series of new fractions all of which were tested by nitration and found to yield large quantities of nitro compounds with the following melting points.

TABLE 106

B.P. of Fraction, °C.	Nitro Compound, M.P., °C.
152–155	80– 87
155–159	86
159–160	81– 90
160–168	85– 87
172–200	80–110

The data show that *mesitylene* was present in considerable amount in all fractions.

An attempt was made to determine whether *pseudocumene* was present in the portion boiling at 160 to 168° since previous work had shown that isomers of mesitylene were formed during the cracking of acetone at 500°. From this fraction was obtained a sulph-amide melting at 141–142° which proved to be a derivative of mesitylene. Thus, it seems that mesitylene was the main aromatic constituent of the fraction boiling from 152 to 200°.

A portion of the gas obtained in the cracking of acetone was passed into a solution of bromine in acetic acid. Thus, 169 g. of bromide was obtained which consisted of 20 g. of ethylene bromide and bromides of higher olefins. These were distilled under diminished pressure and a small amount of a crystalline bromide melting at 37° and another melting at 73–76° were separated. According to carbon-hydrogen analysis and bromine determination, these crystals were the tetra- and penta-bromides of acetone, respectively. Because of the wide boiling range of the liquid bromides and also because of the small amounts obtained, these products were not studied in detail.

Nine hundred and forty-six grams of hydrocarbon obtained by the cracking of acetone, under the conditions specified, was distilled three times in order to determine its composition and ascertain the characteristics of the components.

The analysis and the results obtained with one of the fractions are presented in the following table.

TABLE 107

FRACTION No.	B.P., °C.	AMOUNT, G.	d^{15}_{15}	n^{20}_{D}	% C	% H
1	45– 75 [a]	6.0	0.6914	1.3902	84.63	15.28
2	57– 90	9.0	0.7054	1.4000		
3	90–100	34.0		1.4093		
4	100–110	126.0	0.7229	1.4130	85.60	14.67
5	110–120	34.5		1.4195		
6	120–130	14.0	0.7478	1.4262	85.60	14.35
7	130–140	4.0		1.4358		
8	140–150	7.5	0.7927	1.4490		
9	150–160	26.0		1.4712		
10	160–170	362.5	0.8573	1.4875		
11	170–180	3.5		1.4820		
12	180–200	5.0	0.8404	1.4795		
13	50– 90 [b]	14.0	0.8498	1.4799		
14	90–100	11.5		1.4875		
15	100–110	18.5	0.8705	1.4925	88.44	11.65
16	110–120	24.5		1.4960		
17	120–130	12.5	0.8816	1.4987		
18	130–140	22.5		1.5089	88.58	11.45
19	140–150	19.0	0.9120	1.5146		
20	150–160	18.0		1.5183		
21	160–170	16.5	0.9280	1.5208	88.34	11.41
22	170–180	5.5		1.5245		

[a] Fractions 1–12 distilled at 760 mm.
[b] Fractions 13–22 distilled at 13 mm.

As previously stated, the chief fraction (10) was pure mesitylene which was obtained in 25% yield calculated on the acetone taking part in the reaction (50% of the acetone was recovered unchanged). The total amount of hydrocarbons obtained represented a 60% yield.

In order to investigate the character of the hydrocarbons contained in the first fractions, 50 g. of the fourth fraction, which was practically insoluble in 80% sulphuric acid, was hydrogenated in the presence of nickel oxide at 200°. The hydrogenated product distilled between 95 and 105°, had an odor similar to that of gasoline, did not decolorize potassium permanganate solution, did not react with nitrating mixture, and was not brominated in the presence of aluminum bromide according to the method of Gustavson. Therefore, the hydrogenated product was a mixture of paraffin hydrocarbons, a fact also shown by its analysis.

Anal. Found: C, 84.4; H, 15.9.

Fractions 18 and 19 were combined (total 30 g.) and hydrogenated under the same conditions. In contrast to the hydrogenation of the fourth fraction, this hydrogenation did not go to completion. The product was washed with sulphuric acid and distilled over sodium. It had the odor of petroleum and a wide boiling range: 120–265° (760 mm.).

Anal. Found: C, 88.1; H, 12.3; d_{20}^{20}, 0.8660; n_D^{19}, 1.4910.

Treatment with bromine according to the method of Gustavson, in contrast to the behavior of the hydrogenated product of the fourth fraction, gave a liquid bromide indicating that the hydrogenated product possessed naphthenic characteristics.

Fraction 20, boiling at 150–160°, and fraction 21, boiling at 160–170° (13 mm.) were also hydrogenated. Analysis of the chief fraction of the hydrogenated product (b.p., 120–140°, 12 mm.) gave the following: C, 90.3; H, 10.9; n_D^{20}, 1.5364.

This fraction dissolved in sulphuric acid to the extent of 60%. Therefore, the high boiling unsaturated hydrocarbons in the distillates do not hydrogenate at 200° under pressure to any appreciable extent.

Thus, it is possible to explain the structure of the low boiling hydrocarbons obtained by the cracking of acetone in the presence of zinc chloride. These hydrocarbons are principally olefins of isostructure. The fraction boiling at 150–200° consists chiefly of *mesitylene.* Regarding the fractions distilling between 200 and 300°, the question of their structure is still open at present. It is assumed that in all probability they consist of polymerization products of diolefins and of secondary products formed by the action of high temperature and pressure upon the latter.

CRACKING OF DERIVATIVES OF BENZOIC ACID [1]

In an investigation conducted by Ipatieff, Orlov, and Petrov concerning the alkylation of phenol (refer to chapter on alkylation), it was assumed that the formation of alkyl phenol might be explained by the isomerization at high temperature and pressure of the first formed ether. In the present chapter, an attempt is made to explain the influence of temperature and pressure upon certain derivatives of benzoic acid.

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[1] Ipatieff, Orlov, and Petrov, Bull. soc. chim., *39*, 664 (1926).

According to Cahours,[1] heating the methyl ester of salicylic acid with barium oxide produces anisole and barium carbonate. Similarly Cahours [2] and Cahours and Baly [3] claim that heating the ethyl ester of salicylic acid with barium oxide gives phenetole.

In order to determine the ability of barium oxide for the removal of carbon dioxide, the methyl and ethyl esters of salicylic acid were heated in the high pressure apparatus in the absence of barium oxide. On heating at 340–350° for 2–3 hours, there was obtained a large yield (up to 70%) of anisole and phenetole, respectively. The residue consisted of a phenol and a small amount of tarry products. The pressure registered 170 atmospheres, and in some experiments, in order to obtain a still higher pressure, hydrogen was pumped in at the beginning of the reaction. It was found that increase in pressure did not necessarily influence the yield of the products formed in this reaction. Analysis of the gas gave the following: CO_2, 64%; CH_4, 33%; CO, 1%. Thus, the removal of carbon dioxide took place in the absence of barium oxide and the rôle of this oxide in the reaction of Cahours and Baly must be attributed to the formation of non-volatile barium phenolate and the consequent greater stability of this product at the reaction temperature.

In order to continue the study of the effect of high temperature upon other derivatives of benzoic acid, the methyl esters of salicylic acid and of para-methoxybenzoic acid were prepared by passing hydrogen chloride into a solution of the corresponding acid in methyl alcohol.

The action of heat was different upon the two isomeric esters indicated above. *Methyl salicylate* remained practically unchanged on heating at 400–420° for 4 hours, whereas heating the ester of para-methoxybenzoic acid at the same temperature for 2 hours resulted in a change in molecular arrangement, accompanied by deep-seated decomposition. Carbon dioxide, as well as a large amount of ethylene, was found in the reaction gas and the apparatus contained carbon and tarry products from which ether extracted a small quantity of anisole and unchanged methyl p-methoxybenzoate.

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[1] Cahours, Compt. rend., *41*, 69 (1855); *43*, 65 (1856); *52*, 327 (1861); *74*, 218 (1872).

[2] Cahours, Compt. rend., *74*, 314 (1872).

[3] Cahours and Baly, Compt. rend., *70*, 269 (1870).

Next, phenyl salicylate (salol), orthonitrobenzoic acid and its barium salt, and para-nitrobenzoic acid were subjected to the action of high temperatures.

The heating of salol in the high pressure apparatus at 400–420° for 2 hours gave xanthone, phenol, and small amounts of diphenyl ether as indicated by Graebe.[1] It should be mentioned that diphenyl ether was always formed in the distillation of salol at ordinary pressure.

Identical products were obtained when orthonitrobenzoic acid or its barium salt was heated with water in the presence of alumina at approximately 310° for 2 hours. In each case there was obtained a small amount of nitrobenzene (2–3%) together with carbon and tarry products. When subjected to the same experimental conditions, para-nitrobenzoic acid gave only traces of nitrobenzene, the greater part of the para-nitrobenzoic acid being converted into carbonaceous material.

Decomposition of Salts of Aromatic Sulpho-Acids under Pressure [2]

The question of the regeneration of hydrocarbons from aromatic sulpho-acids and their salts by the action of steam at ordinary pressure was studied by Armstrong,[3] Friedel and Crafts,[4] Kelbe [5] and Fournier.[6] Wilson and Meyer [7] showed that a number of sulpho-acids and their salts decompose and regenerate the aromatics when steam is passed through a mixture of the sulpho-acid (or its salt) and an excess of sulphuric acid. Different temperatures are required for the decomposition of different sulpho-acids. Kelbe found that the method of Armstrong for bromsulphonic acids leaves much to be desired; however, he obtained good results in this case by decomposing the bromsulphonic acids with superheated steam. Also, he showed that free sulphonic acids (but not their salts) may be decomposed with steam without the addition of sulphuric acid.

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[1] Graebe and Eichengrun, Ann., *269*, 323 (1892).

[2] Ipatieff and Petroff, Ber., *59*, 1737 (1926).

[3] Armstrong, J. Chem. Soc., *45*, 148 (1884).

[4] Friedel and Crafts, Compt. rend., *109*, 95 (1889).

[5] Kelbe, Ber., *19*, 92 (1886).

[6] Fournier, Bull. soc. chim., (3) 7, 652 (1892).

[7] Wilson and Meyer, Ber., *47*, 3160 (1914).

Friedel and Crafts modified the method of Armstrong by replacing sulphuric acid with phosphoric acid, since when using sulphuric acid it is impossible to avoid the formation of mono- and disulphonic acids. Both of these acids are very stable, and their formation lowers the hydrocarbon yield. Thus, for example, if a temperature of 170° is required for the decomposition of benzene sulphonic acid, then for the decomposition of benzene disulphonic acid it is necessary to increase the temperature up to 300° and even then only a part of the compound is hydrolyzed.

Friedel and Crafts found a difference in the ease of decomposition of various salts in the regeneration of diethylbenzene from the corresponding sulphonic acid at 150–170°. Fournier found that the salts of barium and cadmium gave insignificant amounts of hydrocarbon whereas salts of the alkali metals gave excellent results. Very little data are to be found regarding the hydrolysis of sulpho-acids under pressure.

In working with sodium hydroxide, a competition of two reactions was observed: (1) decomposition into hydrocarbon and sulphate, and (2) decomposition into phenol and sulphide. The first reaction is predominant in the decomposition of phenol sulphonic acids, as well as of chlorobenzene sulphonic acid.

Assuming that water should be able to hydrolyze rapidly at high temperature, a systematic study was made of the decomposition of various salts of sulphonic acids in the presence of alumina catalyst in the high pressure apparatus. The experimental results revealed that a whole series of sulphonates may be decomposed completely by the action of water alone. The experimental data are summarized in the table shown on pages 438–439.

The mechanism of the decomposition of sulphonic acids may be considered to consist in two phases. In the first phase, as indicated by Expts. 6 and 7, the salt hydrolyzes to give free sulphonic acid and metal oxide; in the second phase a decomposition of sulphonic acid into hydrocarbon or phenol and sulphuric acid takes place.

Alumina plays an active rôle in the first phase, but in the decomposition of the sulpho-acids themselves, as indicated in Expts. 38 and 39, alumina does not act catalytically.

The temperature at which decomposition of the salts of the sulpho-acids begins is quite high, varying between 200 and 480°. The temperature gradients in "fractional hydrolysis" are more sharply defined than indicated by Armstrong. Thus, for example, the difference between the optimum hydrolysis temperatures of phenolsulphonic acid and of chlorobenzene sulphonic acid is 55°, but under the specified conditions the difference between these temperatures for the corresponding sodium salts (Expts. 4 and 19) is 140°.

The temperature at which hydrolysis began varied, depending on the character of the sulphonic acid and of the metal with which it was combined (Expts. 6–11 and 33–41). The influence of the metal on the decomposition temperature of various sulphonic acids was different. Thus, sodium sulphanilate and phenol-sodium sulphonate were decomposed completely at 300°; barium sulphanilate gave no aniline at 380°, while phenol-p-barium sulphonate decomposed easily at 250°. Some sulphonates did not decompose under any condition, (Expts. 21–30) for example, sodium xylene sulphonate, sodium naphthalene-beta-sulphonate, and the sodium salt of naphthol-(1)-sulphonic acid-(4). Apparently a primary hydrolysis took place at such a high temperature and the free sulphonic acid decomposed.

If a comparison be made of the hydrolysis of salts of sulphonic acid under high pressure with the decomposition of free sulphonic acids at ordinary pressure, there are certain similarities in addition to the differences previously mentioned. The high temperature of hydrolysis of sodium benzene sulphonate (Expts. 18 and 19) is decreased by the introduction of a hydroxyl or an amino group into the benzene nucleus (Expts. with sodium phenol sulphonate and sodium sulphanilate) and is increased by the introduction of acid groups or of halides (Expts. 42–45).

The sodium salts of fourteen sulphonic acids, barium sulphanilate and the barium, iron, and copper salts of phenol sulphonic acids were investigated in the present study. The results obtained merely anticipate the results which will be obtained by further study of the decomposition of various salts of sulphonic acids under pressure. In all probability this method will make possible the separation of hydrocarbons whose boiling points are close together.

All experiments were made in the high pressure apparatus. In the experiments with the copper salts, the charge was placed in a glass liner inserted into the bomb in order to avoid the displace-

TABLE 108

HYDROLYSIS OF SALTS OF AROMATIC SULPHONIC ACIDS AT HIGH TEMPERATURES AND PRESSURES

EXPT. NO.	SALT	SALT, G.	WATER, G.	Al_2O_3, G.	TIME OF HEATING, HRS.	MAX. TEMP., ° C.	PRESS., ATMS.	REACTION PRODUCTS	% YIELD
1	Sodium p-Phenolsulphonate	50	50	5	1.5	400	110	Phenol	45
2	Sodium o-Phenolsulphonate	50	50	5	3	410	130	Phenol	45
3	Sodium p-Phenolsulphonate	40	50	0	3	300	75	Phenol	60
4	Sodium p-Phenolsulphonate	40	50	4	3	300	85	Phenol	70
5	Sodium p-Phenolsulphonate + 28 g. Sodium Hydroxide	40	80	4	3	420	145	Undecomposed sodium phenolsulphonate	
6	Barium p-Phenolsulphonate	50	50	5	3	275	90	Phenol	65
7	Barium p-Phenolsulphonate	50	50	5	3	250	55	Phenol	70
8	Barium p-Phenolsulphonate	50	50	3	3	200	26	No phenol	
9	Iron p-Phenolsulphonate	50	50	5	2.5	200	28	No phenol	
10	Iron p-Phenolsulphonate	50	50	5	2	230	60	Phenol	60
11	Copper p-Phenolsulphonate	30	60	3	2	200	45		40
12	Sodium o-Cresol Sulphonate	50	50	5	3.5	400	160	o-Cresol	40
13	Sodium p-Cresol Sulphonate	50	50	4	2	400	150	p-Cresol	30
14	Sodium p-Cresol Sulphonate	40	50	4	3.5	280	43	p-Cresol	70
15	Sodium p-Cresol Sulphonate	40	50	4	3	260	30	No p-Cresol	
16	Sodium o-Cresol Sulphonate	40	50	4	2.5	260	33	o-Cresol	10
17	Sodium o- + p-Cresol Sulphonate	40 + 40	100	8	4	260	36	o- + p-Cresol	15
18	Sodium Benzene Sulphonate	30	40	3	5	400	100	$C_6H_5SO_3Na$ After salting out	
19	Sodium Benzene Sulphonate	40	50	4	3.5	440	250	Benzene	70
20	Sodium Toluene Sulphonate	32	40	4	6	380	70	Toluene	65
21	Sodium Xylene Sulphonate	50	40	5	3	340	70	No xylene	
22	Sodium Xylene Sulphonate	50	40	5	2	400	110	No xylene	
23	Sodium Xylene Sulphonate	30	50	3	3.5	460	165	Xylene (partially carbonized)	
24	Potassium m-Benzene Disulphonate	25	50	3	2	360	85	No benzene	
25	Potassium m-Benzene Disulphonate	25	50	3	2	440	170	No benzene	
26	Potassium m-Benzene Disulphonate	40	25	4	3	480	215	Benzene (carbon and gases)	

TABLE 108 *Continued*

Hydrolysis of Salts of Aromatic Sulphonic Acids at High Temperatures and Pressures

Expt. No.	Salt	Salt, G.	Water, G.	Al_2O_3, G.	Time of Heating, Hrs.	Max. Temp., ° C.	Press., Atms.	Reaction Products	% Yield
27	Sodium Beta-Naphthalene Sulphonate	50	50	5	5	360	100	No naphthalene	
28	Sodium Beta-Naphthalene Sulphonate	50	50	5	3	440	180	Naphthalene (partially carbonized)	
29	Sodium Naphthol (1) Sulphonate (4)	40	50	5	3.5	345	80	Undecomposed sodium naphthol sulphonate	
30	Sodium Naphthol (1) Sulphonate (4)	28	80	3	3	440	150	Resin	
31	Sodium Naphthol (1) Sulphonate (4)	25	40	0	3	300		Resin	
32	Sodium Naphthionate	100	100	10	4	300	120	Alpha-naphthylamine + Alpha-naphthol + NH_3	60
33	Sodium Sulphanilate	50	50	5	2.5	400	100	Aniline 1 g. of diphenylamine	50
34	Sodium Sulphanilate	40	50	4	2.5	306	90	Aniline 1 g. of diphenylamine	50
35	Sodium Sulphanilate	40	50	4	2	300	59	Aniline only	70
36	Sodium Sulphanilate	40	50	14	2.5	260	23	No aniline	
37	Sodium Sulphanilate + 25 g. Sodium Hydroxide	40	100	4	3	330	50	No aniline	
38	Sulphanilic Acid	20	40	0	2	250	54	Aniline	60
39	Sulphanilic Acid	20	50	10	2.5	250	44	Aniline	55
40	Barium Sulphanilate	50	50	5	2.5	380	100	No aniline	
41	Barium Sulphanilate	50	50	5	2	440	180	Aniline	40
42	Sodium Chlorobenzene Sulphonate	50	40	5	4	400	100	Traces of phenol	
43	Sodium Chlorobenzene Sulphonate + 20 g. Calcium Oxide	50	50	5	2	470	205	Phenol	12
44	Chlorobenzene + 20 g. Calcium Oxide	30	50	5	2	470	210	No phenol	
45	Sodium Bromobenzene Sulphonate	50	50	5	2	430	150	No phenol	

ment of copper from its salts by the iron walls of the bomb. In the experiments with chloro- and bromobenzene sulphonates, calcium hydroxide was added to protect the iron walls of the autoclave from the action of the hydrogen halide. In many of the experiments equal amounts of salt and water were taken. A considerable quantity of the substance was taken for the investigation in order that the isolation and the identification of the reaction products might not present difficulties. The liquid hydrocarbons and reaction products were separated from water in a separatory funnel, and after drying, were distilled. The phenols, after acidification, were extracted with ether directly from the high pressure apparatus. The reaction products of the sulphanilates were first made alkaline and then distilled with steam. In these latter experiments, at a temperature above 300°, aniline and small amounts of diphenylamine were formed.

The reaction products were pure and the yields at optimum temperatures, considering unavoidable handling losses, were almost quantitative.

CHAPTER IX

CATALYTIC CONDENSATION

This chapter describes experiments on the condensation of various organic compounds in the presence of a number of catalysts. First, attention is to be focused on the catalytic action of alumina. Many investigators have used this catalyst, not only for dehydration, polymerization, and isomerization, but also for condensation. Among these investigators may be mentioned Tchichibabin,[1] Majima, Unno, and Ovo [2] and others. Also investigations on condensation of organic compounds in the presence of hydrochloric and phosphoric acids have been made by Ipatieff.

Since its introduction as a catalyst in organic chemistry by Ipatieff in 1902, alumina has served in many ways particularly in processes of dehydration and isomerization. The monograph on "Alumina as a Catalyst in Organic Chemistry" (1927) (translated into German in 1928) published by Ipatieff gives many illustrations of its former uses.

The condensation reactions catalyzed by alumina have been studied for various classes of organic compounds, such as alcohols, phenols, acids, ketones, etc., and in all these reactions the catalytic action of alumina was based on its ability to take up water to form hydrates which, in turn, decomposes to regenerate the catalyst and to form condensation products.

The first study along this line was the investigation of the condensation products obtained from ethyl alcohol under pressure in the presence of a mixture of iron oxide and alumina.

CONDENSATION PRODUCTS OF ETHANOL [3]

This investigation was undertaken for the purpose of effecting a polymerization under pressure of ethylene *in statu nascendi*, as obtained from ethanol by the action of alumina at a relatively low temperature. Ipatieff [4] had previously shown that at 360° under pressure, ethylene polymerizes into a series of hydrocarbons consisting of olefins, paraffins, and naphthenes. Hydrocarbons of the gasoline boiling range made up about 50% of the liquid product.

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[1] Tchichibabin, J. prakt. Chem., *107*, 129 (1924); Ber., *60*, 1877 (1927).

[2] Majima, Unno, and Ovo, Ber., *55*, 3854 (1922).

[3] Ipatieff and Klukvin, Ber., *58*, 4 (1925).

[4] Ipatieff, Ber., *44*, 2978 (1911).

It was supposed that the ethylene, at the time of its origin from ethanol, polymerizes at a low temperature, giving low boiling hydrocarbons. Thus, it was thought that an opportunity would be afforded to study more intimately the course of this interesting reaction. Experiments confirmed this assumption only in part, because of the complication of the main reaction by condensation reactions catalyzed by the action of the iron walls of the autoclave. This iron, together with alumina, promoted the aldehyde decomposition of ethanol with the formation of aldehyde condensation products.

The reaction was carried out as follows: Ethanol and alumina were placed in the iron tube of the high pressure apparatus which was then heated at 530–540° for 6 hours. The reaction product, obtained after cooling the apparatus and releasing the gas, consisted of two layers both of which contained considerable proportions of oxygen-containing compounds and were more or less soluble in water. The amount of water-soluble material present in the upper layer was 35%; the insoluble portion consisted of hydrocarbons primarily of naphthenic character.

The upper layer was shaken with water until all the water-soluble compounds had been extracted. From the aqueous solution the oxygen-containing compounds were salted out by potash and found to be acetaldehyde, acetone, and isopropyl alcohol. In addition, methylethyl ketone, methylethyl carbinol, and perhaps acetal were separated, especially from the higher boiling fractions. Separation and analysis of these products presented many difficulties because of their properties, and particularly because these substances boil in close proximity to each other. The lower layer of the reaction product also contained considerable amounts of acetone and isopropyl alcohol.

The dehydration of alcohol begins at 400°, whereas the formation of aldehyde from alcohol under the influence of iron requires a temperature of about 500°. It was expected that the formation of aldehyde would not take place and that only ethylene would be formed. Actually, the course of the reaction was entirely different. Under the conditions indicated, catalytic decomposition of alcohol occurred with the formation of aldehyde and the reaction product consisted not only of the hydrocarbons originating from the polymerization of ethylene, but also of oxygen-containing compounds which were nothing else than products of aldehyde condensation under the influence of alumina.

This latter reaction is of special interest because here, more than anywhere else, an analogy exists between the action of inorganic catalysts and that of enzymes. Neuberg discovered a special enzyme in yeast which he called *carbolase.* This carbolase produces the condensation of two aldehyde molecules into keto-alcohol, $CH_3COCHOHCH_3$, a reaction identical with the action of aluminum oxide (see below).

In order to explain the formation of acetone and isopropyl alcohol, as well as of other products, it is necessary to assume that the aldehyde undergoes condensation under the influence of alumina according to the following equations:

$$(1)\ CH_3CHO + CH_3CHO \rightarrow CH_3CH(OH)CH_2CHO$$

$$(2)\ CH_3CHO + CH_3CHO \rightarrow CH_3CH(OH)COCH_3$$

$$(3)\ CH_3CHO + CH_3CHO \rightarrow CH_3COOCH_2CH_3 + H_2O \rightarrow CH_3CH_2OH + CH_3COOH$$

In the first case, aldol formed at a high temperature decomposes similarly to aldehyde into carbon monoxide and isopropyl alcohol, as indicated by the following equation:

$$CH_3CH(OH)CH_2CHO \rightarrow CO + CH_3CH(OH)CH_3$$

In turn, isopropyl alcohol decomposes into acetone and hydrogen under the influence of the iron catalyst, as shown experimentally:

$$CH_3CH(OH)CH_3 \rightarrow H_2 + CH_3COCH_3$$

Also, aldol may be reduced by hydrogen to methylethyl carbinol which, in turn, loses hydrogen giving methylethyl ketone. In the second case, aldehyde may be condensed to form keto-alcohol, which may be easily reduced to methylethyl carbinol and methylethyl ketone.

It would be assumed that the condensation of acetaldehyde proceeds in both directions, but in view of the gas analysis which showed only a small content of carbon monoxide, it is possible that the condensation proceeds only in the second direction.

The formation of acetone and isopropyl alcohol may also be explained in a third manner, namely, the reaction by which acetaldehyde is condensed according to the reaction of Canizzaro and Tischenko, with the formation of ethyl acetate. The acetic acid thus formed under these conditions may be decomposed further into acetone, carbon dioxide, and water at a higher temperature in the presence of alumina as previously indicated by Ipatieff's experiments with acetic acid.

$$2CH_3COOH \rightarrow CO_2 + H_2O + CH_3COCH_3$$

Analysis of the gas remaining in the apparatus at the end of the reaction showed 16–20% of carbon dioxide which is evidence favoring the Canizzaro reaction, though it is difficult to explain the formation of such a large quantity of carbon dioxide by the condensation of acetaldehyde. In all probability, the condensation process proceeds simultaneously in the second and third directions.

It would be interesting to continue the study of this reaction[1] in order to clarify all its details. It would be most desirable to carry it out in the absence of an iron catalyst as well as in the presence of various mixed catalysts.

The details of the experimental procedure were as follows: An iron tube (capacity 480 cc.) was placed in the high pressure apparatus, filled with 80 cc. of ethanol and 6 g. of alumina, and then heated at 530–540° for 6 hours. During the reaction, the pressure reached a maximum of 240–260 atmospheres, which after cooling the apparatus, dropped to 40–42 atmospheres. The reaction product consisted of two layers, the upper yellow in color, the lower completely colorless. From 80 cc. of alcohol was obtained an average of 22 cc. for the upper layer, 30–34 cc. for the lower layer, and 19–20 liters of gas.

Some of the gas analyses are summarized in the following table:

TABLE 109

Date	% CO_2	% C_nH_{2n}	% CO	% O_2	% H_2	% CH_4	% N_2
May 3, 1922	17.6	2.4	5.6	1.0	31.2	41.1	1.1
Sept. 11, 1922	16.0	2.0	6.8	1.2	24.8	49.2	
Sept. 12, 1922	14.0	3.6	6.8	1.2	26.8	49.2	
Sept. 19, 1922	16.8	1.2	4.8	2.0	27.2	46.4	1.6
Jan. 2, 1923	20.8	1.6	2.6	1.2	21.2	53.0	

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[1] The I.G. was issued a patent for the production of acetone and other ketones from alcohol using this reaction.

The high carbon dioxide content can be explained only by the formation of acetic acid, according to the Canizzaro reaction. If it be assumed that 50% of the alcohol was consumed in the formation of aldehyde and that the aldehyde so formed was converted quantitatively into acetic acid and ethanol, then 21 g. of acetic acid would be formed. Calculations from the gas analysis data show that in every experiment an average of about 7–8 g. of carbon dioxide was formed and the quantity of acetic acid corresponding to this amount of carbon dioxide in terms of the catalytic decomposition of acetic acid into acetone, water, and carbon dioxide, is 21 g.

Thus, it appears highly probable that 50% of the alcohol underwent the aldehyde decomposition and that this aldehyde reacted according to the Canizzaro reaction. A certain part of the second half of the alcohol, as well as part of the ethanol again obtained through the Canizzaro reaction, may also have given an aldehyde which condensed with the formation of a keto-alcohol or aldol. The remainder of the ethanol decomposes into ethylene and water under the influence of alumina and almost the entire amount of this ethylene was polymerized into higher hydrocarbons.

Investigation of the Upper Layer.—Thirteen hundred and fifty grams of upper layer decreased in volume about 16% on washing with water. The washed product, 1154 g., was dried with calcium chloride, and distilled through a column into the following fractions: (1) 20–80° (443 g.); (2) 80–150° (390 g.); (3) 150–180° (87 g.); (4) 180–210° (52 g.); (5) 210–240° (30 g.); (6) higher than 240° (35 g.).

A 72% yield of material boiling below 150° was obtained from the water-washed product. All of this yield cannot be considered as consisting of hydrocarbons since it was later learned that certain fractions of the upper layer still contained a considerable amount of water-soluble, oxygen-containing compounds. Also, the distillation loss of this product was high due to the presence of acetaldehyde in the lower fractions.

Further distillation gave the following fractions: (1) 20–60°; (2) 60–80°; (3) 80–100°; (4) 100–125°; (5) 125–150°.

The *first fraction* (b.p., 20–60°) contained considerable acetaldehyde. Bromination of a sample boiling from 30 to 40° established the presence of unsaturated hydrocarbons, especially amylene (up to 25%) since the resulting dibromide distilled at

152–160°. The hydrocarbons remaining after bromination did not decolorize potassium permanganate solution and boiled at 30–32°.

The *second* (b.p., 60–80°) and the *third fraction* (b.p., 80–100°) were treated five times with water (or until there was no further decrease in volume) in order to remove water soluble oxygen-containing compounds. The water insoluble residue was dried with calcium chloride and finally fractionated.

The material extracted by water from the fractions boiling at 60–80° and 80–100° was salted out with potash and distilled. The product distilling at 80–90° had an alcoholic odor, and after drying with barium oxide, it still had the same boiling point. It reacted with sodium and with phosphorus pentachloride and gave the following analytical figures:

Anal. Calcd. for C_3H_8O: C, 60.0; H, 13.3. Found: C, 62.1, 61.5; H, 14.1, 13.3.

From the data obtained it was concluded that the product separated from the aqueous solution was isopropyl alcohol. The high carbon percentage may be explained by the presence of a small amount of methylethyl carbinol and methylethyl ketone, the presence of each being actually proven.

The substance insoluble in water, obtained from the fractions boiling at 60–80° and 80–100°, was distilled through a dephlegmator to give the following fractions: (1) 62–68° (61 g.); (2) 68–74° (22 g.); (3) 74–84° (30 g.); (4) 84–94° (28 g.); (5) 94–104° (53 g.); (6) 104–114° (18 g.).

The fraction boiling at 62–68° contained about 30% of unsaturated hydrocarbons, as shown by treatment with sulphuric acid (*d*, 1.84). The following analysis was obtained:

Anal. Calcd. for C_6H_{12}: C, 85.7; H, 14.3. Calcd. for C_6H_{14}: C, 83.7; H, 16.3 Found: C, 84.8; H, 15.2.

Hydrogenation of this fraction in the presence of nickel oxide under pressure gave a hydrocarbon boiling at 61–66° which did not decolorize potassium permanganate solution; d_0^{15}, 0.688; n_D^{14}, 1.3840.

Anal. Found: C, 84.0; H, 15.8.

These data show that this fraction consisted principally of *hexane* together with 30% of *hexene* and small amounts of naphthenic hydrocarbons.

The fraction boiling at 68–74° contained about 30% of unsaturated hydrocarbons; d_0^{15}, 0.7096; n_D, 1.3940.

Anal. Calcd. for C_6H_{12}: C, 85.7; H, 14.3. Found: C, 84.7; H, 14.8.

The fraction boiling at 84–94° was hydrogenated in the presence of nickel oxide at 240–260°. The resulting product which did not decolorize potassium permanganate solution, was divided by distillation into two fractions: (1) 83–93°; (2) 93–100°. The fraction boiling at 83–93° had d_0^{15}, 0.7024.

Anal. Calcd. for C_7H_{14}: C, 85.7; H, 14.3. Calcd. for C_7H_{16}: C, 84.0; H, 16.0. Found: C, 85.2, 84.9; H, 14.9, 14.9.

The fraction boiling at 93–100° had the following properties: d_0^{15}, 0.7258; n_D^{15}, 1.4010.

Anal. Calcd. for C_7H_{14}: C, 85.7; H, 14.3. Calcd. for C_8H_{18}: C, 84.2; H, 15.8. Found: C, 85.0, 84.9; H, 14.9, 14.9.

Analysis of the hydrogenated product shows that the fraction boiling at 84–94° contained naphthenic hydrocarbons.

The fraction boiling at 94–104° contained about 30% of olefins, as shown by treatment with sulphuric acid (d, 1.84). Hydrogenation of this fraction in the presence of nickel oxide at 260–280° under pressure gave a product which did not decolorize potassium permanganate solution. Distillation divided the product into two fractions: (1) 90–98°; (2) 98–108°.

Anal. Calcd. for C_8H_{16}: C, 85.7; H, 14.3. Found: C, 85.0, 84.9; H, 15.0, 15.1.

Fraction boiling at 98–108°; d_0^{15}, 0.7378; n_D^{15}, 1.4080.

Anal. Found: C, 85.3; H, 14.5, 14.4.

These data indicate the presence of a considerable amount of naphthenic hydrocarbons.

About 25% of the *fourth fraction* (b.p., 100–125°), 196 g., dissolved in water. From the aqueous solution a product was salted out which was distilled and analyzed. (Refer to the following table.)

TABLE 110

Fraction No.	B.P., ° C.	d_0^{15}	% C	% H	Product	d_0^{15}	% C	% H
1	80– 90		58.0 58.1	12.2 13.2	$C_4H_{10}O$	0.8270	64.9	13.5
2	90– 95		62.7 62.4	13.3 13.0	C_4H_8O	0.8125	66.7	11.2
3	95–105		64.5 64.2	13.3 12.9	C_3H_8O	0.786	60.0	13.3
4	105–110	0.8351	66.1 66.3	12.7 13.1	C_3H_6O	0.7994	62.1	10.4

According to the analyses and properties (including the action of metallic sodium and of sodium bisulphite) the fractions investigated consisted chiefly of methylethyl carbinol and methylethyl ketone with an admixture of isopropyl and ethyl alcohols. These products originated from acetaldehyde, the intermediate keto-alcohol being reduced to methylethyl carbinol.

The portion of the fourth fraction which was insoluble in water consisted of hydrocarbons. It was distilled and the proper fractions were combined with the corresponding distillates from the fifth fraction.

The *fifth fraction* (b.p., 125–150°) was treated with water; only a very small part dissolved. The resulting product was combined with the distillates of the fourth fraction and twice distilled. The following fractions were obtained: (1) 108–116°; (2) 116–126°; (3) 126–140°; (4) 140–155°; (5) 155–170°; (6) 170–200°.

Analyses of these fractions gave the folllowing results:

TABLE 111

Fraction No.	B.P., ° C.	d_0^{15}	% C	% H
			C_nH_{2n} = 85.7	14.3
1	80–116		83.9	13.4
			83.9	13.4
2	116–126	0.7960	85.0	14.1
3	126–140	0.7106	85.7	13.8
			85.7	14.3
4	140–155	0.8250	86.0	13.7
			85.9	13.8
5	155–170	0.8328	86.0	13.8
6	170–200		83.2	12.8

The fraction boiling at 170–200° was yellow in color and contained oxygen compounds as well as olefins, but consisted chiefly of naphthenic hydrocarbons.

Investigation of the Lower Layer.—The lower colorless layer (about 2 liters) was salted out with potassium carbonate, dried with granulated potassium carbonate, and distilled through a dephlegmator. The following fractions were obtained: (1) 64–74° (66 g.); (2) 74–78° (150 g.); (3) 78–80° (257 g.); (4) 80–82° (235 g.); (5) 82–89° (78 g.); (6) 89–120° (30 g.).

The fraction boiling at 89–120° was refractionated into two fractions: (1) 90–105°; (2) 105–115° which gave the following analytical data:

Anal. Fraction boiling at 90–105°. Found: C, 61.5, 62.1; H, 13.3, 14.1. Fraction boiling at 105–115°. Found: C, 65.0, 65.3; H, 13.1, 13.2.

Judging from the analytical figures and from the properties, it was assumed that methylethyl carbinol and methylethyl ketone were present. All fractions contained traces of acetaldehyde as shown by the reduction of ammoniacal silver oxide. They did not contain unsaturated hydrocarbons as evidenced by nonreaction with bromine. The first four fractions were heated with freshly precipitated silver oxide under a reflux condenser for several hours to remove acetaldehyde. The contents of the flask were then distilled on a water bath, the distillate was salted out with potash, and the substance was separated and dried. The insoluble silver salt was washed, dried, and analyzed. In all cases it was found to be pure silver acetate.

After the removal of acetaldehyde from the first four fractions (b.p., 64–82°), these fractions were dehydrated in order to test for the presence of acetone and isopropyl alcohol. For this purpose, the products (after drying in the vapor phase) were passed slowly through a copper tube containing alumina at 500°. Under these conditions, acetone remains unchanged, but ethanol and isopropyl alcohol undergo dehydration to ethylene and propylene, respectively. Isopropyl alcohol is decomposed almost quantitatively due to the characteristic ease of dehydration of secondary alcohols. The liquid products obtained by this dehydration were collected in a cooled receiver and the gas was passed into a well-cooled bromine solution which absorbed it completely. The liquid product was salted out with potash, dried, and distilled. Four fractions were obtained, analyses of which are presented in Table 112 on p. 450.

These results, as well as the special tests made for acetone on the first fraction and the alcohol reactions of the three remaining fractions show that in the first fraction (b.p., 57–74°) there was present about 40% of acetone admixed with ethanol and in the balance of the fraction, 94% ethyl alcohol together with a very small amount of isopropyl alcohol.

In order to show the presence of isopropyl alcohol among the reaction products it was necessary to separate propylene bromide from ethylene bromide. The bromides obtained from the gas evolved in the dehydration of the first four fractions (b.p., 64–82°)

TABLE 112

Fraction No.	B. P., ° C.	Analysis	
		% C	% H
1	57–74	55.5	12.5
2	74–77	48.4	13.0
		48.9	12.6
3	77–79	48.5	13.8
		48.6	13.5
4	79–81	49.1	13.5
		49.3	13.6
Calcd. for	Acetone	62.0	10.4
	Ethanol	52.2	13.0
	Ethanol, 94%	49.0	12.9

when distilled at ordinary pressure, began to boil at 85°, and then the temperature rose gradually to 136°, the greater part of the bromides distilling at 136–146°. The bromides remaining in the distillation flask solidified to a crystalline mass which after recrystallization melted at 116–118°. This product was butadiene tetrabromide.

The liquid bromide was redistilled, the main portion coming over at 139–142°. Analyses of the fractions gave the following results:

TABLE 113

Fraction No.	B. P., ° C.	d_0^{15}	% Br
1	131–136		83.1
			83.0
2	136–146	2.0610	82.1
			82.2
3	139–142	2.0401	80.4
			80.5
$C_2H_4Br_2$		2.19	85.1
$C_3H_6Br_2$		1.94	79.2

The analytical figures of the bromide boiling at 139–142° and its properties left no doubt that it was propylene bromide. Consequently, the formation of large amounts of acetone and isopropyl alcohol was due to the decomposition of ethanol in the presence of the mixed catalyst, alumina and iron.

The approximate yield of acetone and isopropyl alcohol under the conditions of the experiment was about 20%.

Up to the present, attempts to determine the yield of reaction products quantitatively have been unsuccessful. However, it may be assumed that polymerization of ethylene takes place under the joint action of alumina and iron catalysts and that it proceeds in such a way as to form large amounts of naphthenic hydrocarbons. The yield of the gasoline fraction was considerably larger than that obtained by the polymerization of ethylene alone.

A thorough investigation of this interesting reaction is far from accomplished. It is necessary to study the results obtained when operating under various conditions, particularly in a continuous process, in order to discover the conditions leading to the formation of all the products obtained.

Condensation of Phenols with Aliphatic Alcohols

The first experiment on the condensation of phenol with alcohol was made with methyl alcohol. In this experiment phenol was heated with methanol in the presence of an alumina catalyst at 440° under a pressure of about 200 atmospheres and o-cresol [1] was formed. Likewise, ethanol with phenol gave ethyl phenol. These reactions will be discussed in the later chapter on alkylation in connection with the alkylation of various organic compounds under the influence of a number of catalysts. But in order to indicate the condensation process responsible for the formation of xanthene the discussion will deal only with the action of methyl alcohol upon phenol at high temperature and pressure.

Condensation of Phenol and Methyl Alcohol: Synthesis of Xanthene.—A series of investigations by a number of scientists (Ipatieff, Fischer, and others) have showed that pressure is a very important factor in chemical reactions. In fact, the course of a given reaction is often entirely different at ordinary pressure from that at high pressure. Therefore, it was interesting to study the influence of pressure upon the reaction described briefly by Briner, Pluss, and Paillard,[2] who showed that the passage of the vapors of phenol and methyl alcohol through alumina at 410–440° resulted in dehydration and condensation (alkylation) reactions leading to the formation of hexamethylbenzene.

The reaction between phenol and alcohol under various conditions has been the subject of numerous investigations. Thus Lieberman [3] showed that p-isobutyl phenol was formed by heating phenol and isobutyl alcohol at 180° under a reflux condenser in the presence of a large amount of zinc chloride. B. Fischer [1] obtained para-tertiary amyl phenol from tertiary amyl alcohol and phenol under similar conditions and Erreza [2] showed that by heating ethanol and phenol at low pressure, para-ethyl phenol and para-ethyl phenetole were obtained.

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[1] Ipatieff, Orloff, and Razuvaev, Bull. soc. chim., *37*, 1576 (1925).

[2] Briner, Pluss, and Paillard, Helv. Chim. Acta., 7, 1046 (1924).

[3] Lieberman, Ber., *14*, 1482 (1881); *15*, 150 (1882).

All these reactions indicate alkylation of the benzene nucleus of phenol, the alkyl radical entering the para position. Likewise, para-alkyl phenols are obtained from alkyl phenyl ethers by the action of aluminum chloride as Hartmann and Gattermann [3] showed with isobutyl phenyl ether from which small amounts of para-isobutyl phenol were obtained.

In our experiments, in which a mixture of phenol and methyl alcohol was heated at 440° in the presence of alumina under a pressure of 220 atmospheres in the high pressure apparatus, the results differed from those of Brimer, Liebermann, and others. Under our experimental conditions, the reaction product consisted of o-cresol, and p- and m-cresol were not observed. Anisole and xanthene were obtained in small amounts, and ethylene, carbon monoxide, hydrogen, and carbon, as well as traces of benzene were also found. The presence of hexamethylbenzene could not be shown. The formation of anisole may be explained as a simple etherification of phenol by methyl alcohol under the influence of alumina, analogous to the reaction of Sabatier and Mailhe [4] in which they used thorium oxide instead of aluminum oxide. Briner obtained only liquid products, among them anisole, when using thorium oxide.

The formation of o-cresol may be explained by the simple alkylation of phenol, but at high temperature and pressure the ortho compound is obtained instead of the para. The formation of o-cresol may also be explained by the isomerization of anisole.

A comparative experiment indicated that under the influence of temperature and pressure, anisole decomposes into phenol, ethylene, and o-cresol. When the methyl ether of o-cresol is heated under the prescribed conditions, the formation of an ortho compound was observed, which is in direct contrast to the results obtained by Hartmann and Gatterman.

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[1] Fischer, Ber., *26*, 1646 (1893).

[2] Erreza, Gazz. chim. ital., *14*, 1484.

[3] Hartmann and Gattermann, Ber., *25*, 3531 (1892).

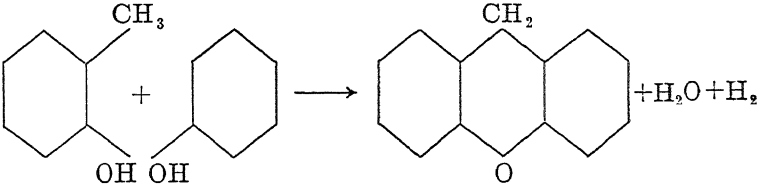
[4] Sabatier and Mailhe, Compt. rend., *151*, 359 (1910).

Various explanations may be given concerning the method of formation of xanthene. Gladstone and Tribe,[1] as well as Möhlan,[2] showed that distillation of aluminum phenolate gave xanthene as one of the products.

$$(C_6H_5O)_3Al \rightarrow 2Al_2O_3 + C + H_2 + CH_4 + C_6H_6 + C_6H_5OH + (C_6H_5)_2O + C_{13}H_{10}O$$

Assuming that under our experimental conditions the same reaction occurs, phenol alone was heated with aluminum oxide and diphenylene oxide and a small amount of diphenyl ether were obtained.

A more probable mechanism, however, is that xanthene results from the interaction of phenol and cresol under the influence of dehydrating substances in the manner of the reaction observed by Graebe,[3] that is, the formation of xanthene from phenols in the presence of aluminum chloride.



An experiment in which a mixture of o-cresol and phenol was heated at 440–450° in the presence of alumina under pressure confirmed this assumption inasmuch as xanthene was found among the reaction products.

All reagents used in the experiments were obtained from Kahlbaum. One part by weight of phenol and six parts by weight of methanol were used in each experiment. The amount of aluminum oxide taken was 1/50–1/60 of the weight of the reaction mixture; the temperature was 420–440°; the maximum pressure, 220 atmospheres; and the duration of heating, 24 hours.

After distilling off the unreacted methanol, 850 g. of product was obtained from the entire series. The material was a dark colored liquid with green fluorescence. It distilled at 90–320° giving 800 g. of distillate and a thick tarry residue. Since the distillate contained unreacted phenol, it was washed with alkali and the hydrocarbon layer extracted several times with ether. The phenolate solution was decomposed with sulphuric acid, the phenol layer separated, dried with sodium sulphate, and distilled through a column. The following fractions were obtained: (1) up to 183° (480 g.); (2) 183–193° (56 g.).

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[1] Gladstone and Tribe, J. Chem. Soc., *39*, 9 (1881).

[2] Möhlan, Ber., *49*, 168 (1916).

[3] Graebe, Ber., *16*, 862 (1883).

The phenol content of the second fraction was about 45%, according to the melting point determined in accordance with the method of Raschig. Judging from its characteristic odor the residue was o-cresol.

Material boiling at 188–193° was separated from the second fraction by distillation. A mixture of 5 g. of this fraction, 20 g. of potassium hydroxide, and a small amount of copper oxide was heated at 210–250° for 2.5 hours and the product was dissolved in water. The solution was acidified with sulphuric acid, and after addition of potassium carbonate, it was extracted four times with ether. After acidifying the aqueous layer with phosphoric acid, it was distilled and salicylic acid was obtained in amounts approximating that of the o-cresol. Thus, the formation of o-cresol was proven, its yield being about 6–7% of the phenol used.

An experiment made for the purpose of testing for the presence of para-cresol by means of the barium salt of its sulphonic acid according to the method of Raschig gave negative results. The ether extract from the hydrocarbon layer was dried with anhydrous sodium sulphate, the ether was removed, and the residue was distilled through a column. The following fractions were obtained: (1) 80–150° (2.5 g.); (2) 150–200° (48 g.); (3) 200–250° (11 g.); (4) 250–320° (22 g.).

The fourth fraction solidified in the receiver to a yellowish-white mass.

The first fraction contained traces of benzene. From the second fraction was separated a portion possessing the characteristic odor of anisole. The determination of the methoxyl number according to Zeisel gave the following data:

Anal. Calcd. for $C_6H_5OCH_3$: OCH_3, 28.7. Found: OCH_3, 27.8.

The fourth fraction was treated with hot alkali and the precipitate was filtered and recrystallized from alcohol. Colorless crystals were obtained which melted at 101° and possessed the characteristic pleasant odor of xanthene. A solution of the substance in concentrated sulphuric acid exhibited a green fluorescence. The following analytical figures were obtained:

Anal. Calcd. for $C_{13}H_{10}O$: C, 85.7; H, 5.5. Found: C, 86.3; H, 5.8.

Behavior of Anisole on Heating.—Anisole, in the presence of alumina, was heated at 440° under a maximum hydrogen pressure of 200 atmospheres for 36 hours. Ethylene was detected in the gas, and unchanged anisole as well as phenol was present in the liquid products. o-Cresol was found in the phenol fraction, its presence being proven by the formation of salicylic acid by the interaction of the phenol, potassium hydroxide, and copper oxide.

Behavior of Phenol on Heating.—Phenol was heated with aluminum oxide at 480–500° under a maximum pressure of 200 atmospheres for 10 hours with the resultant formation of a small amount of hydrogen and a solid material insoluble in alkali. In comparison with preceding experiments, this solid was found to be a mixture of diphenylene oxide and a small amount of diphenyl ether. After several recrystallizations, its melting point was 74°.

The following analytical figures were obtained:

Anal. Calcd. for $C_{12}H_8O$: C, 85.7; H, 4.8. Calcd. for $C_{12}H_{10}O$: C, 84.7; H, 5.9. Found: C, 85.1; H, 5.1.

Besides the products previously mentioned, there was also formed in all the experiments a certain amount of a low melting compound, dark blue in color, soluble in alkali, and dissolving in alcohol to form a dark green solution. Due to lack of material this substance could not be obtained in a pure state and, therefore, its nature was not determined.

CONCLUSIONS

The reaction between phenol and methanol proceeds altogether differently under high pressure than it does at ordinary pressure. For example, under high pressure the alkyl group enters the ortho position of the benzene nucleus of phenol and not the para position as it does at ordinary pressure. Also, a secondary reaction occurs under pressure with formation of xanthene.

CONDENSATION OF LACTIC ACID TO METHYLSUCCINIC ACID UNDER PRESSURE [1]

In preceding work [2] it was shown that hydrogenation of sodium mandelate in aqueous solution in the presence of nickel oxide in the high pressure apparatus, leads to the reduction of the hydroxyl group, and the elimination of carbon dioxide with the formation of a hydrocarbon. It was assumed that this reaction occurs with fatty acids in general. Investigation of the hydrogenation of sodium lactate was made for the purpose of obtaining propionic acid, together with sodium carbonate and methane or ethane. The reaction in this case proceeded, however, in a different manner. Condensation of lactic acid to a dibasic acid, methylsuccinic acid, took place readily under the influence of a mixed catalyst, comprising nickel oxide and alumina. The course of this reaction may be explained as follows: Two molecules of sodium lactate eliminate water to form the disodium salt of dimethyl malic acid. Under these conditions, the disodium salt of dimethyl malic acid was unstable and under the influence of hydrogen and of the catalyst, methyl alcohol was split off and sodium methyl succinate was formed.

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[1] Ipatieff and Razuvaev, Ber., *59*, 2031 (1926).

[2] Ipatieff and Razuvaev, Ber., *59*, 306 (1926).

The main reaction was accompanied by two side reactions: (1) formation of a considerable amount of sodium carbonate and methane (analogous to the formation of hydrocarbons by hydrogenation of sodium mandelate); (2) formation of a series of monobasic acids the presence of which may be readily explained. Propionic acid originated, as it was anticipated, directly from lactic acid. Other acids may have been formed from the dibasic acids by the removal of the COONa group, for example, n-butyric acid from methylsuccinic acid (this reaction also takes place when methylsuccinic acid is exposed to the action of sunlight in the presence of uranium oxide.[1] Methylethyl acetic acid was formed from the hypothetical dimethyl malic acid by the splitting of one carboxyl group and the reduction of the hydroxyl group. The formation of a small amount of high boiling acids is unaccounted for at present and the same is true for the formation of a minute quantity of a pleasant-smelling substance which distilled over a wide temperature range. Considering the odor and certain reactions, it is assumed that this product consisted of a mixture of secondary alcohols and that diethyl carbinol was probably present. Reactions occurring in this process, in which the chief reactions are indicated by dotted arrows, may be expressed by the following scheme:

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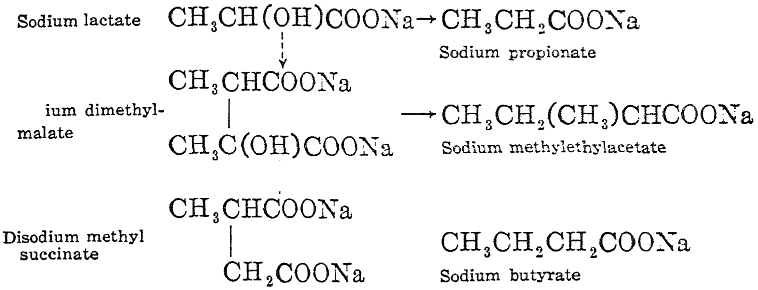
[1] Seecamp, Ann., *133*, 254 (1865).



$$CH_3CH(OH)COONa \rightarrow CH_3CH_2COONa$$

$$\begin{array}{l} CH_3CHCOONa \\ \quad | \\ CH_3C(OH)COONa \end{array} \longrightarrow CH_3CH_2(CH_3)CHCOONa$$

$$\begin{array}{l} CH_3CHCOONa \\ \quad | \\ \quad CH_2COONa \end{array} \qquad CH_3CH_2CH_2COONa$$

Action of Hydrogen under Pressure upon Sodium Lactate Solution in the Presence of Nickel Oxide and Alumina.—The reaction was carried out in a 1000-cc. high pressure apparatus into which was poured a solution of 70 g. of sodium lactate in 75 cc. of water together with 12 g. of a catalyst mixture consisting of equal parts of nickel oxide and aluminum oxide. The bomb was filled with hydrogen at 70 atmospheres pressure. The reaction was run at 270° for about 12 hours, during which time a small decrease in pressure was noted. After cooling, the pressure was 50 atmospheres. Analysis of the gas showed 0.6% of carbon dioxide, 19.2% of methane, and 79.3% of hydrogen.

After removing the clear solution, the apparatus was washed several times with water. No carbonization or resinification was observed in this reaction. The 2 cc. or so of oil floating on the surface of the solution was distilled with steam. It was slightly yellow in color, had a strong but pleasant odor, and boiled over a wide temperature range, 110–240°. Analysis of the oil showed the following: C, 72.1%; H, 11.4%. The salt solution was filtered from the catalyst mixture and evaporated to dryness. The carbonate content was determined by titration. The theoretical amount of sodium carbonate which could be formed from 36.9 g. of sodium lactate was calculated to be 17.4 g.

The salts were dissolved in water and decomposed by the theoretical amount of sulphuric acid. The aqueous solution was evaporated until the separation of sodium sulphate. This was filtered and washed with a small amount of water. The residue was evaporated almost to dryness, when it solidified. For the separation of methylsuccinic acid, the pulverized mass was extracted with ether and the ether was evaporated, leaving a mixture of solid and liquid acids, the latter being removed by drying on a clay plate. The solid was crystallized from benzene. Methylsuccinic acid is only slightly soluble in cold benzene, but readily soluble in hot benzene. Even after many recrystallizations the acid had a low melting point, 105°, instead of 112–115° as indicated in the literature.

Two weighed samples of this acid were titrated with 1/10 *N* alkali using phenolphthalein as indicator. The following data were obtained: 0.1208 g. required 9.16 cc. 1/10 *N* alkali; 0.1212 g. required 9.20 cc. 1/10 *N* alkali. These values correspond exactly to the theoretical.

Methylsuccinic acid has an asymmetric carbon atom and may be resolved into its optical antipodes by means of brucine. By fractional crystallization, well-developed crystals of the d-acid salt were obtained, a single crystal weighing several grams. The d-acid obtained from these crystals melted at 111°. An 8.41% solution of the acid ($d^{21.5}_{21.5}$ 1.019) when placed in a tube 20 cc. long, showed an optical rotation of 0.65°, which is considerably lower than that determined by Fischer.[1]

Anal. Calcd. for $C_5H_8O_4$: C, 45.5; H, 6.0. Found: C, 45.6, 45.6; H, 6.1, 6.1.

The following esters of methylsuccinic acid were obtained:

Diethyl ester—b.p., 217–218°; N^{16}_D, 1.4210; $d^{18.5}_0$, 1.0154.

Anal. Calcd. for $C_9H_{16}O_4$: C, 57.5; H, 8.5. Found: C, 57.2, 57.6; H, 8.7, 8.6.

Dimethyl ester—b.p., 196–198°; $n^{16.5}_D$, 1.4221.

Anal. Calcd. for $C_7H_{12}O_4$: C, 52.5; H, 7.5. Found: C, 53.1; H, 7.5.

The yield of methylsuccinic acid was 15.5 g., i.e., approximately 35% of the theoretical amount.

The solution of salts obtained in the reaction was decomposed with acid and distilled. The monobasic acids yielded propionic and n-butyric acids soluble in water and an insignificant amount (1.5–2 cc.) of oil floating on the surface of the solution. The yield of the sodium salts of monobasic acids varied in different experiments, averaging about 6–7 g., which corresponds to about 10% of the sodium lactate.

The acids were separated into five fractions. The properties and analyses of these fractions and of the methyl esters of fractions 1 and 3 are given in the following table:

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[1] Fischer, Ann., *365*, 18 (1909).

TABLE 114

Fraction No.	B.P., °C.	Substance	n_D^{20}	d_0^{21}	Analysis			
					Calcd.		Found	
					% C	% H	% C	% H
1	138–145	Propionic Acid ($C_3H_6O_2$)	1.3870	0.9851	48.7	8.1	48.3	8.4
2	145–155	Propionic and n-Butyric Acid Mixture	1.3905	0.9694			52.1	9.0
3	160–170	Mainly n-Butyric Acid ($C_4H_8O_2$)	1.3965	0.9535	54.6	9.1	55.0	9.3
4	180–220	Chiefly Methylethyl Acetic Acid ($C_5H_{10}O_2$)	1.4060 @22°	0.9402	58.8	9.8	59.6	9.8
5	200–225		1.4223 @21°				64.1	14.8
Methyl Esters	75– 82	Methyl Propionate ($C_4H_8O_2$)		0.9142 @20°	54.6	9.1	53.4	9.4
Methyl Esters	95–105	Methyl-n-Butyrate ($C_5H_{10}O_2$)			58.8	9.9	57.9	9.9

When only one catalyst was used, nickel oxide, the reaction proceeded similarly, but the yield of methylsuccinic acid was considerably less and the yield of monobasic acids was greater. Methylsuccinic acid obtained in the presence of nickel oxide alone, showed a still lower melting point, 101°, than the acid obtained by the joint action of nickel oxide and alumina.

Action of Hydrogen at High Temperature and Pressure upon Sodium Methylsuccinate in the Presence of Nickel Oxide.—A mixture of 28 g. of the salt and 3 g. of nickel oxide was heated 36 hours in the high pressure apparatus at 280–290° under an initial hydrogen pressure of 60 atmospheres. After cooling the apparatus, the pressure was 3 atmospheres. The salt was extracted with water; the characteristic odor detected in the experiment with sodium lactate was not evident. The solution had an alkaline reaction. It was decomposed with the theoretical amount of sulphuric acid and the results were identical with those obtained with sodium lactate. The reprecipitated methylsuccinic acid, after recrystallization from ether, melted at about 98°. Distillation of the neutral aqueous concentrate with phosphoric acid gave an insignificant amount (0.01 g.) of acid. The composition of this acid could be determined only qualitatively, it was soluble in water, had the odor of butyric acid, and was salted out by calcium chloride.

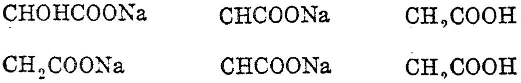
CONDENSATION OF ALPHA-HYDROXY AND ALPHA-KETO-ACIDS BY THE JOINT ACTION OF CATALYSTS [1]

The condensation of sodium lactate by heating with hydrogen under pressure in the presence of a mixed catalyst (nickel oxide and alumina) as described above, suggested that perhaps alpha-hydroxy- and possibly keto-acids might undergo analogous reactions, and experiments with glycollic acid and with pyroracemic acid confirmed this suspicion.

In the condensation of glycollic acid, succinic acid and acetic acid were formed by the reduction of the hydroxyl group, but the principal reaction was the decomposition of the molecule with the formation of carbonate, methane, carbon monoxide, and water. This decomposition was accelerated greatly by increase in temperature. Similar to the result with lactic acid, an oil was obtained with a most decided odor and a wide boiling range. A small amount of high boiling acids also resulted. The reaction may be illustrated as follows:

$$CH_3COONa + H_2O + CH_2OHCOONa \qquad 2CH_4 + CO + 2H_2O + Na_2CO_3$$

$$CH_3COONa + H_2O + CH_2OHCOONa \longrightarrow CH_4 + H_2O + 2HCOONa + CO$$



$$\begin{array}{lll} CHOHCOONa & CHCOONa & CH_2COOH \\ CH_2COONa & CHCOONa & CH_2COOH \end{array}$$

Condensation of pyroracemic acid proceeded much more readily, but in this case it was of great importance not to raise the temperature above 230° else the yield of the chief reaction product, methylsuccinic acid, which was usually about 37% decreased considerably. The first intermediate product obtained in this reaction was lactic acid, which originated from the reduction of pyroracemic acid, the lactic acid condensing as previously indicated.

A solution of 1 mole of sodium glycollate in 100 cc. of water was used for the experiments. The catalyst consisted of a mixture of 5 g. of nickel oxide and 5 g. of alumina. The reaction was carried out in a 375-cc. high pressure apparatus, into which hydrogen was pumped to 85 atmospheres pressure. Condensation proceeded best at temperatures between 220 and 230°. The pressure decreased slowly during 24 hours. At the end of the experiment, the pressure in the cooled apparatus registered 65 atmospheres and the residual gas consisted of: carbon dioxide, 12.5%; methane, 13%; and hydrogen, 74.5%.

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[1] Ipatieff and Razuvaev, Ber., *60*, 1973 (1927).

The salt solution was extracted and the apparatus washed repeatedly with water. An oil (strong odor), which floated on the surface of the solution, was distilled with steam. It was extracted with ether; the ether was evaporated. The residue distilled between 110–170°, the greater part decomposing.

The salt solution separated from the oil was evaporated to dryness, the residue weighed, and the carbonate content determined by titration. The latter varied greatly in amount, depending upon the reaction temperature: it was 72% at 270°; 63% at 255°; and about 50% at 220°.

The salts were redissolved in water, acidified with the theoretical amount of sulphuric acid, and the solution evaporated to incipient crystallization. The solution was separated from the precipitated sodium sulphate by filtration and the residual liquid evaporated almost to dryness. The solid residue was dried and extracted several times with ether. The ether solutions were dried, and the ether was distilled, leaving a small amount of acid which distilled over a wide temperature range, 160–225°, and thus it was impossible to make a more thorough investigation. The acid distilling at 160° had the following composition: C, 61.6%; H, 10.0%.

The remaining acid solution, after extraction with ether, was neutralized with sodium hydroxide and the solution evaporated to dryness, the salt being dried at 140°. The weight of this salt varied, depending on experimental conditions: it was 7.5 g. at 255°; 12 g. at 220°. As a consequence of tests such as cacodyl odor on heating with arsenic trioxide, formation of acetic ester with alcohol and sulphuric acid, and red coloration with ferric chloride, the evidence was that the material was a mixture of sodium acetate and sodium formate.

Removal of the ether left a thick oil (about 6.5 g. at 250°) which solidified on long standing in a dark room. After repeated recrystallization from water, crystals were obtained which were dried on a clay plate and which melted at 167°. When strongly heated the acid sublimed. The properties and analyses of this acid, as well as the formation of pyrrole by heating the ammonia salt, indicated the presence of succinic acid. Its yield was about 6%.

Anal. Calcd. for $C_4H_6O_4$: C, 40.7; H, 5.1. Found: C, 40.9, 39.9; H, 5.0, 5.0.

Condensation of Pyroracemic Acid.—One-half mole of the sodium salt was dissolved in 100 cc. of water in the presence of 5 g. nickel oxide and 5 g. alumina, and the solution was heated at 230° under 90 atmospheres of hydrogen pressure for 24 hours. The pressure was 63 atmospheres at the end of the reaction.

The reaction product, an alkaline solution, was filtered from the catalyst mixture, about 20% of carbonate being found. The strong smelling oil floating on the surface of the aqueous solution was distilled with steam, and the remaining solution was decomposed with the theoretical amount of sulphuric acid and evaporated to dryness. The acid distillate contained a small amount of acids insoluble in water which were not investigated. The ether extract from the dry residue obtained after distilling off the volatile acids gave about 12 g. of an oil which crystallized on standing in a vacuum. After recrystallization from benzene, the acid melted at 107°.

Anal. Calcd. for $C_5H_8O_4$: C, 45.5; H, 6.1. Found: C, 46.0, 45.7; H, 5.9, 6.1.

According to properties, titration, and analyses, the product was methylsuccinic acid.

Reaction with Succinic Acid at 265°.—A solution of 0.33 mole of the acid in 30 cc. of water was heated with 3 g. of nickel oxide and 2 g. of alumina in the high pressure apparatus for 12 hours under an initial hydrogen pressure of 75 atmospheres. At the end of the reaction the pressure had decreased to 63 atmospheres. Analysis of the residual gas showed: carbon dioxide, 6.5%; methane, 4%; and hydrogen, 89.5%.

The thick solution discharged from the apparatus was slightly yellow in color, and rapidly became brown on exposure to air. A strong smelling oil floated on its surface. The content of carbonate was found by titration to be 35%. By acidification with sulphuric acid, a considerable amount of resin was precipitated. The solution was evaporated to dryness and the residue extracted with ether. The ether extract contained about 0.2 g. of methylsuccinic acid which, after recrystallization from benzene, melted at 100°.

Condensation of Polybasic Alpha-Hydroxy Acids in the Presence of Mixed Catalysts [1]

In previous work on the condensation of acids, it was shown that alpha-hydroxy acids condense to dibasic acids in the presence of nickel oxide-alumina catalysts under hydrogen pressure, giving a series of monobasic acids. In the present work the action of the same catalysts upon dibasic and tribasic and upon mono- and dihydroxy acids, such as malic, tartaric, and citric acids was investigated.

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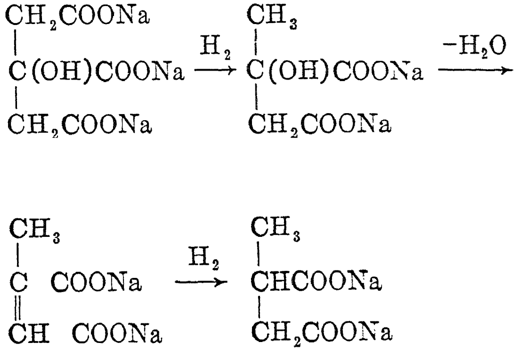
[1] Ipatieff and Razuvaev, Ber., *60*, 1971 (1927).

The experiments indicated that in these cases two reactions take place: (1) reduction of the hydroxyl group with the formation of the corresponding saturated polybasic acid, and (2) splitting of these acids into monobasic acids. The first reaction was observed for the first two acids with formation of succinic acid, but in widely different amounts. Malic acid gave about 50% of succinic acid, whereas the yield from tartaric acid was very small. Evidently, in the latter case, the reason for the small yield is the presence of a second hydroxyl group which interferes with the normal course of the reaction. Decomposition of the sodium salts of the acids yielded formic acid, acetic acid, sodium carbonate, and methane.

Reduction of the hydroxyl group in citric acid with formation of the corresponding tribasic acid was not observed due to concurrent side reactions illustrated by the following equations:



$$\begin{array}{l} CH_2COONa \\ | \\ C(OH)COONa \\ | \\ CH_2COONa \end{array} \xrightarrow{H_2} \begin{array}{l} CH_3 \\ | \\ C(OH)COONa \\ | \\ CH_2COONa \end{array} \xrightarrow{-H_2O}$$

$$\begin{array}{l} CH_3 \\ | \\ C\ \ COONa \\ \| \\ CH\ \ COONa \end{array} \xrightarrow{H_2} \begin{array}{l} CH_3 \\ | \\ CHCOONa \\ | \\ CH_2COONa \end{array}$$

The yield of methylsuccinic acid was rather high, 30%. Simultaneous elimination of carbon dioxide and water took place on dry distillation of citric acid to form itaconic acid,[1] together with other products.

Sodium Malate.—A solution of 0.3 mole of salts in 100 cc. of water was heated 24 hours with 5 g. of nickel oxide and 3 g. of alumina at 250° in a 375-cc. high pressure apparatus under an initial hydrogen pressure of 100 atmospheres. At the end of the reaction, the pressure had decreased to 58 atmospheres. Analysis of the residual gas showed: carbon dioxide, 4%; methane, 10%; hydrogen, 86%.

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[1] Crasso, A., *34*, 61 (1840).

The solution was alkaline and contained an average of 10% of carbonate. This carbonate was decomposed by the theoretical amount of sulphuric acid, the sodium sulphate crystals were filtered, the mother liquor was distilled until further crystallization began, and the residue was evaporated to dryness.

The residue, dried in vacuum, was washed with ether and the acid content in the distillate determined by titration. This was found to be about 27%. The total amount of acid distillate was neutralized with alkali and evaporated to dryness. The residue consisted of a mixture of the salts of formic and acetic acids.

From the ether extract of the solid residue 22 g. of an oil was obtained which crystallized on standing in a vacuum. The acid separated from the oil, after several recrystallizations from water, melted at 184°. Analysis gave the following data:

Anal. Calcd. for $C_4H_6O_4$: C, 40.7; H, 5.1. Found: C, 40.6; H, 5.0.

Titration, analysis, and properties indicated that the product was succinic acid. Its yield was about 50%, the greater part of which was lost on recrystallization.

Sodium Tartrate.—A solution of 0.2 mole of salt in 100 cc. of water was heated 24 hours with 5 g. of nickel oxide and 3 g. of alumina at 245–250° under an initial hydrogen pressure of 85 atmospheres. The pressure decreased to 62 atmospheres at the end of the reaction. Analysis of the gas remaining in the autoclave showed: carbon dioxide, 8%; methane, 7.5%; and hydrogen, 84.5%.

By titration the alkaline solution was found to contain about 25% carbonate. The carbonate was decomposed by the theoretical amount of sulphuric acid and the solution was treated in the same manner as was that from sodium malate. The acid solution which distilled over contained about 20% of volatile acids, chiefly formic acid.

After distilling the formic and acetic acids, 18 g. of a thick oil was obtained from the ether extract of the residue. The ammonium salt prepared from a part of this oil was heated with zinc dust and pyrrole was formed, as shown by the color reaction with pine shavings. The formation of pyrrole confirmed the presence of succinic acid in the oil. On long standing in a vacuum, only a very small amount of succinic acid crystallized. These crystals were pressed on a porous plate and after recrystallization from water, the material melted at 185°.

Anal. Calcd. for $C_4H_6O_4$: C, 40.7; H, 5.1. Found: C, 40.7; H, 5.0.

That part of the acid was heated with 10 parts alcohol and sulphuric acid to form the diethyl ester of succinic acid, boiling point 215–218°; n_D^{20}, 1.4256; d_0^{20}, 1.0430.

Anal. Calcd. for $C_4H_6O_4$: C, 55.1; H, 8.1. Found: C, 55.7, 55.6; H, 8.0, 8.1.

Sodium Citrate.—A solution of 0.2 mole of salt in 100 cc. water was heated 36 hours with a catalyst mixture of nickel oxide and alumina at 250–260° under an initial hydrogen pressure of 60 atmospheres. At the end of the reaction, the pressure had decreased to 35 atmospheres, and the residual gas consisted of: carbon dioxide, 2.0%; methane, 5.7%; hydrogen, 92%.

The amount of carbonate present as determined by titration averaged about 25%. After decomposition of the solution with the theoretical quantity of sulphuric acid, the acid distillate consisted of about 25% of formic and acetic acids, as well as higher acids which were readily extracted with ether. These were not investigated further.

Methylsuccinic acid was extracted from the residue by ether after distilling off the volatile acids. Its yield, 8 g., was about 30% of the theoretical. After several recrystallizations from benzene, in which it was readily soluble hot but sparingly soluble in the cold, an acid was obtained.

Anal. Calcd. for C_5H_8O: C, 45.5; H, 6.1. Found: C, 45.3; H, 6.0.

Condensation of Alpha-Hydroxy-n-Butyric Acid and Alpha-Hydroxy-Isovaleric Acid under the Action of Mixed Catalysts [1]

It had previously been shown that alpha-hydroxy acids can be condensed to dibasic acids under high hydrogen pressure in the presence of a mixed catalyst (nickel oxide and alumina) at 250–270° and it seemed interesting to determine whether this condensation was common to all alpha-hydroxy acids. Accordingly, experiments were made with alpha-hydroxy-n-butyric acid and alpha-hydroxy-isovaleric acid. Experiments showed that the condensation reactions were more complex the longer the carbon chain. Condensation of alpha-hydroxy-n-butyric acid produced a dibasic acid identical in properties and analyses with the sym-methylethyl-succinic acid described by Zelinsky and Bytschichin.[1] It is difficult to explain the mechanism of the formation of this acid. Perhaps the hydroxy-butyric acid condenses normally at the beginning, but later the side chains split off. The latter process takes place often in catalytic processes at high temperature.

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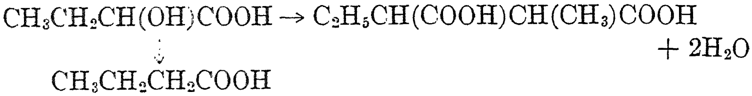
[1] Ipatieff and Razuvaev, Ber., *61*, 634 (1928).



$$\begin{array}{l} CH_3CH_2CH(OH)COOH \rightarrow C_2H_5CH(COOH)CH(CH_3)COOH \\ \qquad\qquad \downarrow \hfill + 2H_2O \\ \qquad CH_3CH_2CH_2COOH \end{array}$$

About 10% of the initial material contributed to the formation of the dibasic acid, while about 25% gave the normal product of reduction of alpha-hydroxy-n-butyric acid. In addition, higher boiling monobasic acids were formed probably by the elimination of the carboxyl group from the dibasic acids formed by condensation.

Alpha-hydroxy-isovaleric acid did not condense under the conditions described above, but the carboxyl group split off to such an extent that a 40% yield of carbonic acid and a considerable amount of formic acid were formed. The absence of higher monobasic acids indicated that no condensation occurred analogous to the one previously indicated. Isobutyl alcohol, formed by the splitting of the carboxyl group, was separated in considerable quantity from the reaction product:

$$(CH_3)_2CHCH(OH)CO_2H \rightarrow (CH_3)_2CHCH_2OH + CO_2$$

Furthermore, saturated acids were found among the reaction products. Propionic acid, separated as a basic lead salt, was formed by the destruction of the carbon chain with liberation of methane, which was present in considerable amount in the gases formed during the reaction. An attempt was made to separate the normal reduction products of isovaleric acid in a pure state but without success. The high boiling acid fraction (145–155°) consisted chiefly of propionic acid admixed with isovaleric acid. Butyric acid was not found among the reaction products.

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[1] Zelinsky and Bytschichin, J. Russ. Phys. Chem. Soc., *21*, 385 (1889).

Sodium Alpha-Hydroxy-n-Butyrate.—A solution of 0.25 mole of the sodium salt in 100 cc. of water was heated at 280–290° in the presence of 5 g. of nickel oxide and 3 g. of alumina in the high pressure apparatus under 70 atmospheres initial hydrogen pressure. After the experiment had continued for four days the pressure had decreased to 65 atmospheres. The residual gas contained 35% of methane and 65% of hydrogen. In some cases the apparatus was opened after 1.5 to 2 days, fresh catalyst added, and the experiment continued. This accelerated the reaction and improved the yields. The salt solution was removed from the apparatus and boiled a short time to eliminate the small amount of oil floating on its surface. The carbonate content as determined by titration was about 20%.

The solution was decomposed with the theoretical amount of sulphuric acid and the precipitated acid was filtered. The filtrate was evaporated until crystallization of sodium sulphate had taken place, but it still retained the solid acid. The filtrate was then evaporated further until only the dry salt remained. The solid acid was extracted from the sodium sulphate with ether in which it is readily soluble and about 25 g. of crude acid was obtained which melted at 170–173°. This acid after crystallizing from water melted at 175–176°, the yield being about 10%.

According to properties, titration, and analysis, this acid was sym-methylethylsuccinic acid.

Anal. Calcd. for $C_7H_{12}O_4$: C, 52.5; H, 7.5; mol. wt., 160. Found: C, 52.4, 52.8; H, 7.4, 7.5; mol. wt., 162–164.

The evaporated aqueous solution was shaken several times with ether, the ether was evaporated, and the acid mixture was distilled into the following fractions: (1) 160–165° (4.5 g.); (2) 165–195° (3 g.). The first fraction, boiling at 160–165°, consisted of n-butyric acid, its yield being about 25% of the theoretical; d_0^{25}, 0.9573; n_D^{25}, 1.3947.

Anal. Calcd. for $C_4H_8O_2$: C, 54.5; H, 9.2. Found: C, 54.2; H, 9.0.

The second fraction, boiling at 165–195°, was not investigated.

Sodium-Alpha-Hydroxy Isovalerate.—A solution of 0.25 mole of the sodium salt in 150 cc. of water was mixed with 3 g. nickel oxide and 2 g. alumina and heated 48 hours at 285–295° under 80 atmospheres initial hydrogen pressure. After the apparatus had cooled, the pressure was 50 atmospheres. Analysis of the residual gas gave: 1.2% of carbon dioxide; 45.2% of methane; and 54.2% of hydrogen.

The solution contained considerable oily layer which was distilled with steam. This liquid which was found to be pure isobutyl alcohol was extracted with ether and distilled, about 5 g. distilling at 108–110°. Its phenylurethane melted at 79–81° instead of at 80°. Its analysis gave:

Anal. Calcd. for $C_4H_{10}O$: C, 64.8; H, 13.6. Found: C, 63.8, 63.9; H, 13.6, 13.5.

The amount of carbonate formed in the solution as a product of acid decomposition was determined by titration to be about 43%. The solution was decomposed with the theoretical amount of sulphuric acid and distilled until only the dry salt remained. Glauber's salt was separated by filtration. The acid distillate was shaken several times with ether and the ether removed by evaporation, leaving about 1.5 g. of an acid boiling at 113–145° and 4.5 g. of an acid boiling at 145–155°. The amount of propionic acid contained in both fractions was determined by precipitating the acids in the form of its basic lead salt according to the method of Haberland.[1] To prove the presence or absence of butyric acid in the second fraction, an attempt was made to prepare its calcium salt, but the experiment showed that no butyric acid was present.

CONDENSATION OF ACETONE AT HIGH TEMPERATURES AND PRESSURES[2] I

Previous study[3] showed that acetone when heated in an iron tube decomposes chiefly into carbon monoxide and a saturated hydrocarbon, and it was further observed that small amounts of unsaturated liquid products were formed. While hydrogenating acetone in the presence of copper oxide and zinc, Ipatieff and Balatchinsky[4] found that unsaturated by-products were formed, but principally in the presence of larger amounts of zinc than of copper oxide.

By passing acetone over alumina at 350°, Senderens[5] obtained carbon monoxide, carbon dioxide, ethane, and a liquid boiling below 200° which was shown to contain mesityl oxide and phorone. These substances are not the only products of acetone condensation. By using various condensation agents, isophorone, xylitone, etc., were also obtained.[1] Furthermore, mesitylene is formed by the action of sulphuric acid upon acetone, a change which takes place only when crude acetone is used in the reaction.[2]

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[1] Haberland, Zeit. anal. Chem., *38*, 217 (1899).

[2] Ipatieff and Petroff, Ber., *59*, 2035 (1926).

[3] Ipatieff, Ber., *37*, 2979 (1904).

[4] Ipatieff and Balatchinsky, J. Russ. Phys. Chem. Soc., *43*, 1760 (1911).

[5] Senderens, Bull. soc. chim., (4), *3*, 824 (1908).

Reckleben and Scheiber,[3] who recommended passing a mixture of acetone and methanol over alumina at 400° for the preparation of hexamethylbenzene, assumed that mesitylene was formed primarily from acetone, but they did not base this assumption on experimental evidence and therefore the question is open as to whether the condensation of acetone to mesitylene is possible under the conditions indicated. According to observations of Greene,[4] various unsaturated hydrocarbons, as well as hexamethylbenzene, but no mesitylene, are obtained when acetone is heated with zinc chloride. Similar observations were made by Senderens [5] when passing acetone over alumina, the presence of mesitylene among the reaction products not being confirmed.

In order to determine the influence of high temperature and pressure upon the course of condensation of pure acetone, a series of experiments was made with pure acetone in the presence of various catalysts. Catalysts such as alumina, zinc chloride, hydrochloric acid, and phosphoric acid were used. The reaction temperature varied from 160–350°, and the maximum hydrogen pressure used was 200 atmospheres. The results obtained were as follows:

(1) Mesitylene is the chief product of this condensation and its yield by this reaction is considerably larger than by the action of sulphuric acid upon acetone.

(2) Aromatic and terpene hydrocarbons of different molecular weights and composition are also formed to a considerable extent.

Anal. Found: C, 88.4, 88.6; H, 11.7, 11.5.

(3) Only very little mesityl oxide is formed, although it is the chief product in the presence of various condensing agents such as hydrogen chloride and others under ordinary conditions.

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[1] Stadtler, Ann., *111*, 279 (1859); Kachler, *ibid.*, *164*, 78 (1872); Binner, Ber., *15*, 588 (1882).

[2] Bielefeld, Inorg. Dissert. Gottingen, 1880.

[3] Reckleben and Scheiber, Ber., *46*, 2364 (1913).

[4] Greene, Bull. soc. chim., (2), *32*, 422 (1879).

[5] Senderens, *loc. cit.*

(4) Solid phorone is not found (perhaps only a trace of isophorone).

(5) Hexamethylbenzene is not formed.

Thus, high temperatures and pressures, as well as continuous contact of acetone and its condensation products with the catalyst, cause a different course of reaction in that the acetone is first dehydrated and then condensed to form hydrocarbons only. The question to be considered is whether hydrocarbons analogous to mesitylene originate by direct condensation of acetone molecules under the influence of alumina, or whether a polymerization of ethylene hydrocarbons (formed from acetone) to naphthenic and other hydrocarbons takes place. In order to answer this and other questions pertaining to the structure of the hydrocarbons formed, the mechanism of the reaction, etc., it was necessary to repeat the experiments on a much larger scale.[1]

For these experiments, water-free acetone was used as obtained from Kahlbaum. After distillation through a dephlegmator over potassium permanganate it boiled at 56.5°. As catalysts, alumina and zinc chloride were used. In a few experiments zinc dust and calcium oxide were added in amounts of 5 to 10% by weight of the acetone taken for reaction.

The duration of heating varied between 2 and 54 hours; the temperature, between 300 and 500°. At the end of the experiment the excess acetone was distilled on a water bath; the reaction product was decomposed with water, and the oil that separated was dried with sodium sulphate. The results obtained are summarized in Table 115.

As the condensation products obtained with alumina and zinc chloride were similar in odor, boiling point, and specific gravity, they were combined for further investigation. Fractional distillation of 345 g. of the composite resulted in the following fractions: (1) 120–150° (90 g.); (2) 150–170° (62 g.); (3) 170–210° (72 g.); (4) 210–310° (95 g.); (5) Residue (25 g.).

In order to determine whether the condensation products contained the ordinary products, mesityl oxide, phorone, and others, these fractions were redistilled and the following fractions obtained: (1) 128–131°; (2) 163–167°; (3) 188–195°; (4) 205–210°; (5) 248–253°; (6) 300–310°.

The fraction boiling at 163–167°, corresponding in boiling

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[1] Ipatieff and Petrov, Ber., *63*, 2806 (1930).

TABLE 115

Expt. No.	Catalyst	T., ° C.	Time of Heating, Hrs.	Press., Atms.	Yield of Condensation Product in Volume Per Cent of Acetone	
					Charged	Decomposed[a]
1	Alumina	500	2	160	12.5	25
6	"	390	15	80	12	30
7	"	480	4	200	17	24
8	"	360	24	112	19	47
9	"	330	54	90	15	40
20	Calcium Oxide	450	2	150	11	21
13	Zinc Dust	480	2	160	17	42
14	" "	300	14	90	10	37
15	Zinc Chloride	460	2	190	35	39
16	" "	340	16	135	41	43
17	" "	300	2	90	25	60
18	" "	300	4	80	30	50
21	" "	400	6	150	40	50
22	" "	320	18	120	40	45

[a] At high temperature, a part of the acetone is converted into tar and gases.

point to mesitylene, was distilled over metallic sodium. The molecular weight of all fractions was determined by Raoult's method, and the refractive index was determined by an Abbé refractometer.

Mesitylene was the chief reaction product. As proof that this hydrocarbon was actually mesitylene, its dinitro compound was prepared according to Fittig,[1] m.p., 86°. Fractions 1 and 3 might consist of a mixture of mesityl oxide, phorone, and hydrocarbons but since the third fraction did not solidify in a cooling mixture, phorone was absent. The analytical data, molecular weight, and boiling range of the third fraction indicated that it consisted to a considerable extent of hydrocarbons $C_{10}H_{14}$, which Haltmeyer [2] had found in the residue obtained when preparing mesitylene by the action of sulphuric acid upon acetone.

Fractions 4 and 5 consisted apparently of isophorone and xylitone mixed with hydrocarbons. The inability to prepare the oxime of i-phorone from the fraction boiling at 210–240° was due perhaps to the presence of large amounts of admixed hydrocarbons as stated by Korp and Müller.[3]

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[1] Fittig, Ann., *141*, 133 (1867).

[2] Haltmeyer, Z., 689 (1867).

[3] Korp and Müller, A., *290*, 140 (1896).

TABLE 116

Comparison of Physical Constants of Fractions of Acetone Condensation Products with the Physical Constants of Known Substances

Fraction or Substance	B.P., ° C.	d_{25}^{25}	Mol. Wt.	Refr. Index		Analysis, Found	
				n_D @	° C.	% C	% H
No. 1	128–131	0.828	102	1.4351	24	76.3	11.2
						76.4	11.0
Mesityl Oxide	128.4	0.854	98	1.4439	20	73.4	10.1
No. 2	163–167	0.857	120	1.4850	23.5	90.1	10.4
						89.9	10.7
Mesitylene	163	0.862	120	1.4911	20	89.9	10.1
No. 3	188–195	0.871	136	1.4774	22.5	84.7	10.8
						84.6	11.2
Phorone	195	d_4^{29} 0.877	138	1.4949	29	78.3	10.1
$C_{10}H_{14}$	193–195		134			89.5	10.5
No. 4	205–210	0.896	148	1.4860	22.5	82.6	10.8
						82.6	10.9
Isophorone	205–210	0.925	138			78.3	10.1
No. 5	248–253	0.922	177	1.5060	22.5	84.4	10.7
						83.8	10.7
Xylitone	251–252	d_4^{16} 0.936	178			80.9	10.1
No. 6	300–310		219	1.5280	22	88.3	10.8
						88.4	10.7

Fraction 6 was practically a pure hydrocarbon. It is interesting to note that this fraction closely approached dixylitone (obtained by Rinner) [1] in boiling point, 310–320° under ordinary pressure. In order to determine whether other hydrocarbons besides mesitylene are formed under the specified experimental conditions and also to determine their respective amounts, the intermediate fractions boiling at 140–160° and 260–300° were distilled over sodium. As anticipated, the fraction boiling at 260–300° reacted feebly with the metal. The colorless distillates boiled at 154–164° and 250–290°, respectively. These fractions had the following properties and analyses.

TABLE 117

B.P., ° C.	n_D @	° C.	Analysis, Found	
			% C	% H
154–164	1.4758	23.5	88.4	11.7
250–290	1.5157	22	88.6	11.5

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[1] Rinner, Ber., *15*, 588 (1882).

The analytical data and other properties indicated that admixture of naphthenes in the lower fractions of hydrocarbons was insignificant, and that under the specified experimental conditions chiefly aromatic and terpenic hydrocarbons resulted. The presence of terpenic hydrocarbons was confirmed by the following reactions:

(1) Fractions boiling at 154–164° and at 250–290° formed tar on treatment with nitric acid.

(2) A mixture of acetic and sulphuric acids imparted a red coloration to the fraction boiling at 154–164°, and a red-brown coloration to the fraction boiling at 250–290°.

It is interesting to note that the fraction boiling at 250–290° on treatment with nitric acid gave a strong odor of musk, but it is not certain as to what compound the odor was due. The literature contains data concerning the formation of artificial musk by the action of nitric acid upon compounds of the terpenic series; for example, from a rectified succinic oil,[1] as well as from compounds of the aromatic series such as butyl xylene.[2]

The hydrocarbons obtained under the experimental conditions amounted to 70% of the condensation products.

CONDENSATION OF ACETONE AT HIGH TEMPERATURES AND PRESSURES[3] II

From preceding investigation[4] it was concluded that acetone condenses readily under certain conditions of temperature and pressure in the presence of various catalysts, such as alumina, zinc chloride, and others to form condensation products consisting chiefly of mesitylene and hydrocarbons of the terpene series.

In order to obtain more detailed data, the present work was undertaken on a larger scale by heating acetone at a constant temperature in the presence of an alumina catalyst. Besides obtaining mesitylene and other hydrocarbons as a result of the condensation of acetone, mesityl oxide and isophorone were separated. Xylitone and sesquiterpenes were also isolated from the condensation product. In their properties the sesquiterpenes resembled the hydrocarbon obtained by Knoevenagel and Beer[5] as a byproduct in the preparation of phorone.

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[1] Elsner, J. prakt. Chem., (2), *26*, 97 (1882).

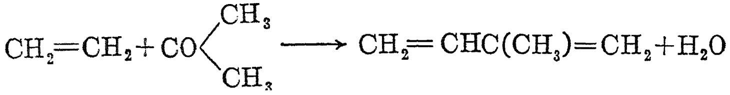
[2] Battegay and Kappler, Bull. soc. chim., (4), *35*, 989 (1924).

[3] Ipatieff and Petrov, Ber., *60*, 753 (1927).

[4] Ipatieff and Petrov, Ber., *59*, 2035 (1926).

[5] Knoevenagel and Beer, Ber., *39*, 3457 (1906).

Aliphatic compounds, such as mesityl oxide and phorone [1] are formed on passing acetone over alumina at 350° at ordinary pressure, a reaction analogous to the condensation of acetone at ordinary temperature and pressure in the presence of hydrochloric acid.[2] On the contrary, at 350° under high pressure, mesityl oxide, mesitylene, isophorone, and xylitone are formed from acetone in the presence of alumina. With the exception of mesityl oxide, the origin of these cyclic compounds is analogous to that of those obtained by the condensation of acetone at ordinary temperature in the presence of calcium oxide.[3] An explanation of the origin of the hydrocarbons of the terpene series may be traced, in all probability, to the condensation of acetone in the presence of ethylene which is always present among the reaction products. The possibility of such a condensation is embodied in a patent by Matthews and Stange [4] according to which ethylene and acetone condense with the formation of isoprene.



$$CH_2{=}CH_2 + CO\begin{matrix} CH_3 \\ CH_3 \end{matrix} \longrightarrow CH_2{=}CHC(CH_3){=}CH_2 + H_2O$$

Of course, the isoprene must undergo polymerization to terpenes and diterpenes under the specified experimental conditions.

In concluding this series of experiments, an experiment was made on the condensation of acetone with methanol in the presence of alumina under pressure. The condensation product consisted of an oxygen-containing compound which darkened on exposure to air and differed from the products obtained by the condensation of acetone alone, in that it gave no semicarbazone. According to Reckleben and Scheiber,[5] hexamethylbenzene should be formed from acetone and methyl alcohol in the presence of alumina at ordinary pressure, but it was not present in the condensation products obtained.

In each of the experiments which were carried out in a high pressure apparatus of 1-liter capacity, 400 cc. of acetone and 10 g. of alumina were heated at 350–400° for 10 to 12 hours under a maximum hydrogen pressure of 100 atmospheres. At the end of the reaction, the pressure was 5 atmospheres. Analyses of the residual gas averages as follows: carbon dioxide, 11%; C_nH_{2n}, 10%; carbon monoxide, 21%; methane, 36.6%.

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[1] Senderens, Bull. soc. chim., (4), *3*, 824 (1908).

[2] Kasanzew, J. Russ. Phys. Chem. Soc., *7*, 173 (1875); Claisen, Ann., *180*, 4 (1876).

[3] Bredt, Ann., *299*, 166 (1898).

[4] Matthews and Stange, Brit. pat., 29,566, Dec. 17, 1909.

[5] Reckleben and Scheiber, Ber., *46*, 2363 (1913).

From 400 cc. of acetone about 340 cc. of a dark liquid was obtained, consisting of 200 cc. of unchanged acetone which was removed by distillation and about 120 cc. of condensation products. The acetone distillate was again subjected to condensation conditions so that practically all the acetone was converted into condensation products of which more than two liters were collected altogether. After washing the condensation product with water, a preliminary fractionation showed that the chief reaction product was mesitylene (about 30%), followed in order of yield, by mesityl oxide and isophorone. The products were distilled, first at ordinary pressure and finally under vacuum for the higher fractions.

The following fractions were investigated:

TABLE 118

B.P., ° C.	° C. @ Mm., Hg	Analysis, Found		Analysis, % Calcd.		
		% C	% H	For	C	H
129–131	760	73.1	10.4	$C_6H_{10}O$	73.4	10.1
		73.2	10.7			
87– 89	11	78.5	10.4	$C_9H_{14}O$	78.3	10.1
		78.6	10.5			
126–128	11	82.0	10.0	$C_{12}H_{18}O$	80.9	10.1
		82.1	10.0			

Semicarbazones were obtained from all the fractions. The semicarbazone of the first fraction boiled at 129–131° (760 mm.) and melted at 156°. Therefore, this fraction consisted of mesityl oxide. The second fraction whose boiling point (87–89° at 11 mm.) corresponded to that of isophorone, gave a semicarbazone which melted at 158°. The third fraction (b.p., 126–128° at 11 mm.) formed a semicarbazone only partially and an oil was left in the residue. According to the analytical data a mixture of isoxylitone and a hydrocarbon was present. Therefore, the fraction distilling at 120–135° under 11 mm. pressure was redistilled over metallic sodium. The distillate boiled at 122–127° at 10 mm. pressure and at 250–260° at ordinary pressure. It had the odor of caryophyllene; n_D^{17}, 1.527.

Anal. Calcd. for $C_{15}H_{24}$: C, 88.2; H, 11.8; mol. wt., 204. Found: C, 87.6; H, 11.5; mol. wt., 194.

The sesquiterpene obtained by Knoevenagel had the following properties and analysis: b.p., 127–128° (10 mm.); n_D^{16}, 1.533.

Anal. Found: C, 87.2; H, 11.9; mol. wt., 192.

Nitration of the fraction boiling at 122–127° (10 mm.) produced a yellow, amorphous substance soluble in alkalies to which it imparted a red coloration. This substance, which had a musk-like odor, was separated from the alkali solution by acids as a yellow mass. When heated, the yellow substance puffed up without melting.

CATALYTIC CONDENSATION OF ACETONE AND OTHER KETONES UNDER THE INFLUENCE OF HYDROCHLORIC ACID [1]

The condensation of acetone under the influence of catalysts and dehydrating agents at various temperatures has already been discussed in detail by a number of investigators.[2] Freer and Lachmann [3] saturated acetone with dry hydrogen chloride and observed the formation of low boiling oxygen-containing condensation products, for example, phorone and mesityl oxide. At a high temperature Kane obtained products of more extensive condensation, mesitylene being among them. Küster and Stallberg,[4] as well as Noyes,[5] worked out a method for preparing mesitylene in yields of 13.5–17.2% by the action of sulphuric acid upon acetone.

Ipatieff and Petrow [6] discussed in detail the condensation of acetone under the influence of alumina and zinc chloride at high temperature and pressure. The formation of a series of condensation products from members of the sesquiterpene type was observed under the experimental conditions previously described.

In the present study, the principal interest is in the mechanism of the condensation reaction whereby acetone is converted into mesitylene. Observations made by Ipatieff, Jr. in his experiments on the displacement of metals of the fifth group from their chlorides (antimony trichloride and bismuth trichloride) in acetone solution by hydrogen under pressure suggested this investigation. He observed, among other reactions, a far-reaching condensation of the solvent which had no relation whatsoever to the salts used. The fact that condensation occurred on diluting the solutions with water was also very interesting. Because of this latter circumstance, it was assumed that the reaction causing closure of the mesitylene ring, as well as the formation of higher condensation products, was due not merely to the dehydrating action of hydrogen chloride, but must also be ascribed to its catalytic action.

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[1] Ipatieff, Dolgov, and Wolnoff, Ber., *63B*, 3072 (1930).

[2] Kane, Ann. Physik., *44*, 475 (1838); Descude, Ann. Chim. Phys. (7), *29*, 493 (1903); Mannich, Ber., *41*, 574 (1908); Hoffmann, J. Am. Chem. Soc., *31*, 723 (1909); Fittig, Ann., *110*, 32 (1859); Baeyer, Ann., *140*, 297, 301 (1866); Heintz, Ann., *187*, 250 (1877).

[3] Freer and Lachmann, Am. Chem. J., *19*, 887 (1897).

[4] Küster and Stallberg, Ann., *278*, 210 (1894).

[5] Noyes, Am. Chem. J., *20*, 807 (1898).

[6] Ipatieff and Petrow, Ber., *60*, 1956 (1927).

On the contrary, when sulphuric acid is used as condensing agent under the same conditions, intensive condensation occurs with the formation of a series of products containing sulphur. As interest was directed principally to the mechanism of the condensation of acetone to mesitylene, the use of sulphuric acid was avoided because under these experimental conditions the desired reaction was accompanied by side reactions in which sulphuric acid participated.

The choice of mild condensation conditions, and an investigation of the process under varying experimental conditions, made possible the determination of optimum conditions for the preparation of mesitylene. The amount of mesitylene formed in relation to the experimental conditions served as a fundamental criterion for determining the course of the reaction. It must be noted that an increase in temperature leads to the formation of more complex condensates as would be expected. The presence of products containing oxygen was observed only at low temperatures. High molecular weight condensation products were observed in all cases, but they were not investigated thoroughly; their quantity was estimated, and their composition approximated. It was established that the high molecular weight condensation products were very similar to those obtained by Ipatieff and Petrow [1] by the condensation of acetone in the presence of zinc chloride. With a given quantity of acetone always charged into the high pressure apparatus and heated at 100–200° in the presence of hydrochloric acid, determinations were made regarding the influence of the following factors on the yield of mesitylene: the amount of aqueous hydrochloric acid added, the temperature, and the duration of the reaction. Hydrochloric acid of 1.19 specific gravity was used as the condensing agent. It was found that the percentage of acetone condensed increased parallel with increase in the concentration of hydrochloric acid in the acetone. However, the course of the reaction changed in the direction of the formation of high boiling oxygen-free products with diminution in the yield of mesitylene. This phenomenon can be readily understood because the ability of hydrochloric acid to cause condensation decreases with dilution. The curve for the formation of mesitylene changed curvature showing that a hydrochloric acid concentration of 5% by volume is optimum for the preparation of mesitylene.

Figure 32 shows the relation between the yield of mesitylene and the concentration by volume of hydrochloric acid at 175° under an initial pressure of 100 atmospheres. The upper curve expresses the percentage yield of mesitylene calculated on the total quantity of acetone used; the lower curve expresses the percentage yield of mesitylene based on the amount of acetone consumed in the reaction.

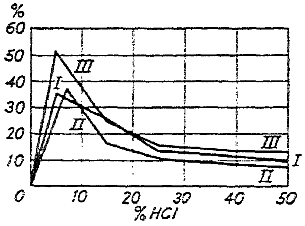

FIG. 32

The formation of mesitylene is rapid, and a certain amount of low boiling oxygen-containing condensation products is formed when the hydrochloric acid concentration is less than 5%. With 5 to 50% hydrochloric acid concentrations there is a gradual decrease in the yield of mesitylene and the formation of higher terpene-like condensation products.

TABLE 119

RELATION OF MESITYLENE YIELD TO HYDROCHLORIC ACID CONCENTRATION

(P, 100 Atms.; T., 175° C.; Time, 24 Hrs.)

Hydrochloric Acid (d, 1.19), % by Vol.	% Yield of Mesitylene Based upon Acetone		Acetone Converted into Mesitylene, % of Total Charged	Acetone Not Consumed in the Reaction, % of Total	Mesityl Oxide, %	Acetone Converted into Mesityl Oxide, % of Total Charged
	Consumed	Charged				
0.0	0	0				
2.5	25	10	28.05	21	0.3	0.43
5	36	36	52.56	0.2	0.0	0.0
15	25	17	24.6	20	0.5	0.59
25	14	11	16.0	25	2.5	3.6
40	12	10	14.6	20	0.0	0.0
50	10	10	14.6	9	0.0	0.0

The observed relation between the formation of mesitylene and the concentration of hydrochloric acid partly explains the poor yield of mesitylene obtained by saturating acetone with gaseous hydrogen chloride. With the higher concentrations of condensing agent the yield may be only 10 to 12%. This agrees with data found in the literature. The results obtained are summarized in Table 119.

After determining the optimum acid concentration, the relation between yield and temperature was investigated.

TABLE 120

RELATION BETWEEN YIELD OF MESITYLENE AND TEMPERATURE
(P, 100 Atms.; HCl, 5%; Time, 24 Hrs.)

T., ° C.	% Yield of Mesitylene Based upon Acetone		Acetone Converted into Mesitylene, % of Total Charged	Acetone Not Consumed in the Reaction, % of Total	Mesityl Oxide, %	Acetone Converted into Mesityl Oxide, % of Total Charged
	Consumed	Charged				
100	2	1.0	1.46	60	2.5	2.9
125	16	7.7	11.2	25	1.3	1.5
135	32	20	29.2	45	1.0	2.9
140	43	29	41.9	55	1.3	1.6
150	41	23	33.58	21	0.0	0.0
175	36	36	52.56	0.2	0.0	0.0
250	20	20	29.2	1.0	0.0	0.0

Plotting the results summarized in Table 120, it was found that the curve (Fig. 33) for the mesitylene yield calculated on the amount of acetone consumed changes in curvature at 140°, going through a maximum. When the mesitylene yield is calculated with reference to the total amount of acetone charged, the peak of the curve lies at 170°.

At 175–190°, both upper and lower curves coincide, indicating that the total amount of acetone undergoes change. A decided decrease in the yield of low boiling oxygen-containing condensation products (mesityl oxide) with increase in temperature indicates the formation of high boiling condensation products due to more sharply defined reaction conditions.

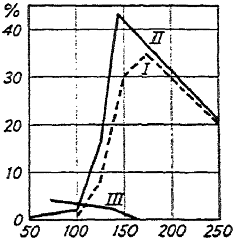

FIG. 33

Considering the course of the reaction with reference to time, it is observed that under optimum conditions (5% concentration of hydrochloric acid, and 145°) there is no further increase in the yield of mesitylene after 24 hours. The results obtained are summarized in Table 121.

TABLE 121

RELATION OF MESITYLENE YIELD TO THE DURATION OF THE REACTION

(P, 100 Atms.; HCl, 5%; T., 145° C.)

TIME OF REACTION	% YIELD OF MESITYLENE BASED UPON ACETONE		ACETONE CONVERTED INTO MESITYLENE, % OF TOTAL CHARGED	ACETONE NOT CONSUMED IN THE REACTION, % OF TOTAL	MESITYL OXIDE, %	ACETONE CONVERTED INTO MESITYL OXIDE, % OF TOTAL CHARGED
	Consumed	Charged (Total)				
3	7	1.0	1.46	90.0	4.5	6.6
10	25	6.6	9.6	75.0	4.0	5.8
16	36	16.0	23.3	50.0	3.0	4.3
20	41	23.0	33.58	21.0	0.0	0.0
24	46	24.1	35.0	50.0	5.0	7.3
30	46	24.1	35.0	50.0	2.9	4.2

Referring to Table 121 and Figure 34, it is evident that the yield of mesitylene is dependent upon the duration of the reaction, and that the velocity of the reaction decreased gradually. As this series of experiments was made under very mild experimental conditions, only about 3 to 4.5% of mesityl oxide (appearing as the first condensation product) could be isolated. In all cases this is in complete agreement with the experiments of Claisen and Jacobson.[1] These investigators found that mesityl oxide and phorone appear as intermediate products in the formation of mesitylene by the action of sulphuric acid on acetone, a reaction which gives other condensation products also. According to these data, the condensation reaction can be considered as consisting of two successive stages with the possible formation of phorone.

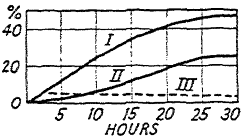

FIG. 34

First mesityl oxide is formed which may be condensed to mesitylene with a new molecule of acetone. Under the specified experimental conditions this mesitylene is more or less stable at temperatures up to 150°, but above this temperature it decomposes completely. However, it is not impossible for three molecules of acetone to combine to form mesitylene.

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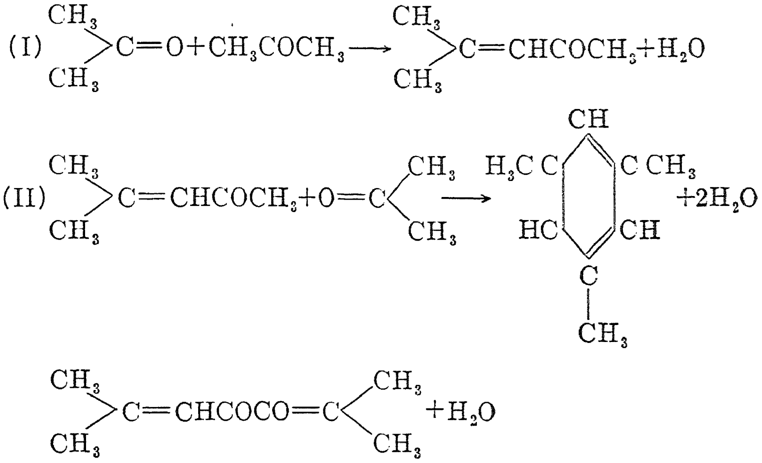
[1] Claisen and Jacobson, Ber., *10*, 858 (1877).



$$\text{(I)}\quad (CH_3)_2{>}C{=}O + CH_3COCH_3 \longrightarrow (CH_3)_2{>}C{=}CHCOCH_3 + H_2O$$

(II)

$$(CH_3)_2{>}C{=}CHCOCO{=}C{<}(CH_3)_2 + H_2O$$

The absence of phorone among the condensation products indicates that either it does not form under the existing experimental conditions or that it quantitatively undergoes further condensation forming more complex products.

Using the results of this investigation on the relation of mesitylene yield to the volume concentration of hydrochloric acid, temperature, and duration of the reaction, it was possible to obtain under optimum conditions between 140 and 150°, a 43% yield of mesitylene calculated with reference to the amount of commercial acetone consumed in the reaction. About 50% of the acetone charged was recovered unchanged. However, there was no loss since the acetone which did not take part in the reaction could be processed again. At 175–180°, practically all the acetone charged took part in the condensation reaction whereby 36% mesitylene was formed. Previously, it was possible to obtain only 17.5% mesitylene.

Two hundred cc. of acetone and 10–20 cc. of hydrochloric acid (*d*, 1.19) was heated at 100 to 200° under a hydrogen pressure of 100 atmospheres. Although the effect of hydrogen pressure on the course of the reaction is not known (experiments conducted under nitrogen pressure did not show any appreciable difference), nevertheless this method has the advantage of simplicity and little waste. The liquid poured from the bomb was yellow and separated into two layers. The lower layer was a mixture of water, hydrochloric acid, and unchanged acetone, while the upper layer consisted of mesitylene and sesquiterpene. The total content of the bomb was cautiously neutralized with dry potash, the aqueous layer saturated with salt and separated from the upper layer, and the latter was distilled. After removal of the acetone, the temperature increased rapidly and the mesitylene fraction distilled between 160 and 180°. By further fractionation the mesitylene content was raised to 80–88%. In some experiments, at lower temperature and with shorter time, a fraction boiling at 120–140° was obtained. This was collected and weighed in a tarred vessel and its composition determined. It consisted of 91% of mesityl oxide mixed with acetone and higher boiling material. The residue boiling above 170° was weighed directly without further distillation. After further fractionation the mesitylene fraction was found to contain up to 88% of pure mesitylene having the following constants: d^{15}_{15}, 0.8660; $n^{21.5}_D$, 1.4928; molecular weight, 118, 122 (in benzene); boiling point, 163.5° (according to micro methods).

Anal. Calcd. for C_9H_{12}: C, 90.0; H, 10.0. Found: C, 90.3, 90.1; H, 9.8, 10.0.

For the purpose of further identification, two derivatives were prepared: namely, dinitromesitylene, m.p., 83°, by nitration in acetic acid; and tribrommesitylene, m.p., 221° (one recrystallization).

Mesityl oxide was identified by the following properties: b.p., 129–130°; mol. wt., found 96, 100, 97 (in benzene), (calcd., 98). These constants agree with those found in the literature.

The condensation products boiling at 200–300° and higher at normal pressure gave the following fractions after double distillation at 30 mm.: (1) 40–142°; (2) 142–146°; (3) 147–150°; (4) 150–160°; (5) 160–161°; (6) 270–274°; (7) 274–276°.

Evidently, the first fraction was a mixture. It was not investigated thoroughly because of the small amount.

The second fraction was a pale yellow oil with an agreeable odor similar to that of camphor; $n^{21.5}_D$, 1.5150.

Anal. Found: C, 88.3; H, 11.3; mol. wt., 206, 208.

The third fraction was also a yellow oil but with a somewhat disagreeable odor; $n^{21.5}_D$, 1.5215.

Anal. Calcd. for $C_{15}H_{24}$: C, 88.2; H, 11.8; mol. wt., 204. Found: C, 88.5; H, 11.2; mol. wt., 206.

The fourth fraction, obviously a mixture, was not investigated thoroughly because of the small quantity obtained.

The fifth fraction had $n_D^{21.5}$, 1.5258.

Anal. Found: C, 88.2; H, 11.6; mol. wt., 208; 216 (benzene).

The sixth fraction was a yellow, odorless oil with $n_D^{20.4}$, 1.5306 and molecular weight, 230 (in benzene). Because of the small amount of material obtained no analysis was made.

The seventh fraction had $n_D^{20.4}$, 1.5306 and molecular weight, 230 (in benzene). This substance was not sufficiently pure to be analyzed.

It is remarkable that the molecular weights of the first, second, and fifth fractions were almost identical. Therefore, isomeric compounds belonging to the same class should be present. The same was true for the sixth and seventh fractions. None of these fractions, however, contained oxygen (sodium test). A more thorough investigation of the substances composing these fractions was discontinued because of their relation to products previously studied by many investigators and also due to the difficulty in handling such small amounts of material containing little known compounds.

CONCLUSIONS

(1) The completeness of the condensation of acetone in the presence of an aqueous solution of hydrochloric acid depends upon the temperature, the concentration of hydrochloric acid, and the duration of the reaction.

(2) An increase in temperature and in concentration is required for the formation of higher molecular weight condensation products.

(3) A method was devised for the preparation of mesitylene in 43% yield calculated upon the amount of acetone consumed, or 36% yield based upon the total quantity of acetone charged.

Dolgov and Volnov [1] made experiments on the condensation of other ketones, methylethyl ketone, acetophenone, and methylacetophenone in the presence of hydrochloric acid under pressure. This method of condensation may be recommended because, compared with other methods, it considerably shortens the reaction time and also appreciably increases the yields. A series of investigations carried out on the condensation of various ketones showed that strictly definite conditions of temperature and concentration of hydrochloric acid exist for maximum yields of the corresponding derivatives obtained according to the scheme presented below:

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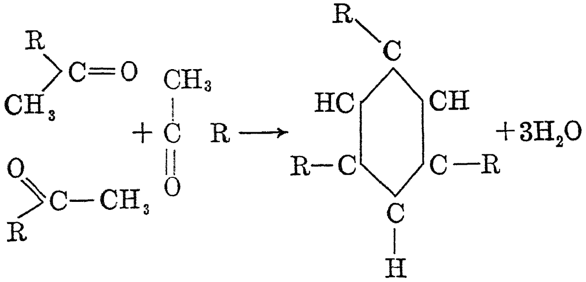
[1] Dolgov and Volnov, J. Gen. Chem. (U.S.S.R.), *1*, 340 (1931).



Thus the amount of acid required increased with increase in the molecular weight of the ketone as indicated in the following table.

TABLE 122

From Ketone	To Hydrocarbon	Requirement of HCl, Volume %
Acetone	30% Mesitylene	4
Acetophenone	30% Triphenylbenzene	46
Methyl Acetophenone	30% Tritolylbenzene	120

Hydrocarbon	Yield, %	Required Concentration of HCl, Volume, %	Time, Hrs.	T., ° C.	Press, Atms.
Mesitylene	46	5	24	140–150	100
1, 3, 5-Triphenylbenzene	35	60	20	100	100
1, 3, 5-Tritolylbenzene	55	160	20	200	100

Pressure accelerates the condensation reaction and aqueous hydrochloric acid is preferable to gaseous hydrogen chloride. By means of this method, good yields of 1, 3, 5-derivatives of aromatic hydrocarbons may be obtained which are difficult to prepare by previous methods.

CONDENSATION OF ALDEHYDES AND KETONES UNDER THE INFLUENCE OF PHOSPHORIC ACID

Phosphoric acid has had very limited application in condensation reactions. In a few cases phosphorus pentoxide is used in alkylation. Nevertheless, phosphoric acid is of interest in a series of reactions which require such substances as sulphuric acid, alumina, zinc chloride, etc. The advantage of phosphoric acid lies in its similarity to alumina; it is a very stable inorganic compound, and it is incapable of oxidizing or sulphonating.

Phosphoric acid is a more active catalyst than alumina and, therefore, effects catalytic processes at lower temperatures. The mechanism of catalytic processes in which this catalyst participates will be discussed in detail in the chapter on the theory of catalytic processes. Here, only experiments on the condensation of aldehydes and ketones will be discussed.

Condensation of Aldehydes with Phenol in the Presence of Phosphoric Acid [1]

Condensation of Benzaldehyde with Phenol.—It is known that sulphuric acid brings about condensation of benzaldehyde with aromatic compounds. However, the data in the literature [2] indicate only a small yield of impure product due to difficulty in separating it from the tars formed in the reaction. Consequently, phosphoric acid was applied to the condensation reaction of benzaldehyde with phenol.

Fifty grams of freshly distilled benzaldehyde (b.p., 179–180°), 100 g. of phenol, and 20 g. of 89% phosphoric acid were used for this experiment. The phosphoric acid was mixed vigorously with the phenol by a motor driven stirrer while the benzaldehyde was added dropwise in an atmosphere of nitrogen. The reaction mixture was kept at 50–60°, and the stirring was continued for 8 hours. No formation of tarry products was observed. At the end of the reaction the entire product was distilled with steam. The distillation was continued until the unchanged benzaldehyde and phenol had been completely removed, leaving the condensation product and a solution of phosphoric acid in the distilling flask. The product (heavier than water) was freed from phosphoric acid by washing with water. It solidified to a crystalline mass, about 50 g. being obtained. This crystalline mass, on recrystallization from hot benzene, gave white crystals melting at 163°.

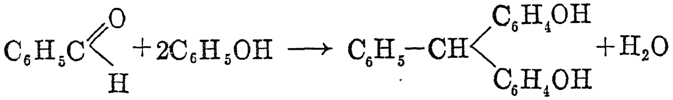
Anal. Calcd. for $C_{19}H_{16}O_2$: C, 82.6; H, 5.8. Found: C, 81.4; H, 6.0.

---

[1] This work was done by Ipatieff and Komarewsky in the laboratories of the Universal Oil Products Company, 1932 and 1933.

[2] Russanow, Ber., *22*, 1944 (1889).

The crystalline product reacted with potassium hydroxide and produced a red coloration. It reacted violently with nitrating mixture. According to its properties and analysis, this substance was dihydroxytriphenylmethane, formed by the following condensation reaction:



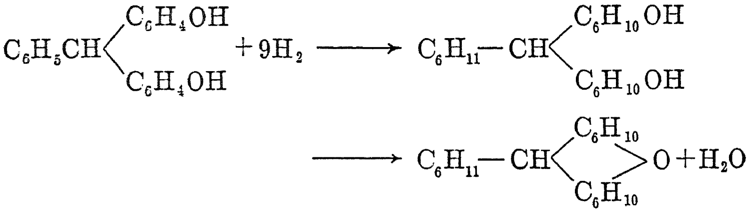
$$C_6H_5C\Big\langle\begin{matrix}O\\H\end{matrix} + 2C_6H_5OH \longrightarrow C_6H_5{-}CH\Big\langle\begin{matrix}C_6H_4OH\\C_6H_4OH\end{matrix} + H_2O$$

To further test the chemical nature of this compound, it was subjected to hydrogenation under pressure in the presence of a nickel oxide—iron oxide catalyst, cyclohexane being added to the mixture to prevent reduction of hydroxyl groups. However, the greater part of it did not go into solution. The hydrogenation proceeded at 275° for 3 hours under an initial hydrogen pressure of 95 atmospheres. At the end of the reaction, the pressure had fallen to 82 atmospheres.

The products obtained were completely soluble in cyclohexane. After distilling off the cyclohexane, the oil boiled chiefly at 265–350° at atmospheric pressure. On standing, it yielded a mass of crystals which after recrystallization from alcohol melted at 106–107°.

Anal. Calcd. for $C_{19}H_{32}O$: C, 82.6; H, 11.6. Found: C, 82.7, 82.6; H, 12.3, 12.3.

Analysis indicated that under the conditions of hydrogenation, one molecule of water had been eliminated from the two hydroxyl groups attached to the two cyclohexyl groups:



$$C_6H_5CH\Big\langle\begin{matrix}C_6H_4OH\\C_6H_4OH\end{matrix} + 9H_2 \longrightarrow C_6H_{11}{-}CH\Big\langle\begin{matrix}C_6H_{10}OH\\C_6H_{10}OH\end{matrix}$$

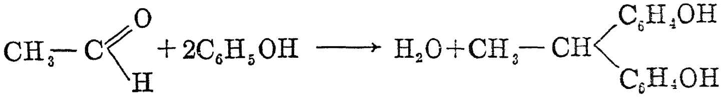
$$\longrightarrow C_6H_{11}{-}CH\Big\langle\begin{matrix}C_6H_{10}\\C_6H_{10}\end{matrix}\Big\rangle O + H_2O$$

Its formation is analogous to the condensation of phenol with resorcinol in the presence of sulphuric acid.

Condensation of Acetaldehyde with Phenol.—The condensation of acetaldehyde with phenol was carried out under the conditions described for the condensation of benzaldehyde with phenol. To a mixture of 50 g. of phenol and 10 g. of 89% phosphoric acid, acetaldehyde was added dropwise with vigorous stirring at 50–60°. Stirring at 50–60° was continued for 8 hours and finally the product of the reaction was steam distilled to remove unchanged acetaldehyde and phenol. Twelve grams of a thick, yellowish oil which did not crystallize on standing remained in the distilling flask. This oil was distilled at 6 mm. and a fraction was collected which boiled at 120–130°. This fraction readily solidified and after recrystallization from hot benzene yielded about 4 g. of crystals melting at 114–115°.

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.5; H, 6.5. Found: C, 77.7; H, 6.6.

According to its properties and analysis this substance is dihydroxydiphenylmethane, having been formed according to the following condensation reaction:



$$CH_3-C\begin{cases}\!=O\\ -H\end{cases} + 2C_6H_5OH \longrightarrow H_2O + CH_3-CH\begin{cases}C_6H_4OH\\ C_6H_4OH\end{cases}$$

Condensation of Ketones with Phenol in the Presence of Phosphoric Acid [1]

The condensation of ketones with phenols has been studied by many investigators, but in almost all cases sulphuric acid was used as the catalyst.

In the present study it was found advantageous to use phosphoric acid as the catalyst.

Condensation of Cyclohexanone with Phenol.—Schmidlin and Long [2] carried out this condensation in the presence of sulphuric acid and obtained 1, 1-diparahydroxyphenyl cyclohexane. In our experiments, a mixture of 49 g. of cyclohexanone and 94 g. of phenol was heated 6 hours at 120–130° in the presence of 30 g. of 100% phosphoric acid. After washing with water, the reaction product was extracted with ether, the ether was evaporated, and the product was finally distilled into the following fractions:

---

[1] This work was done by Ipatieff and Pines in the laboratories of the Universal Oil Products Company, 1933.

[2] Schmidlin and Long, Ber., *43*, 2806 (1913).

TABLE 123

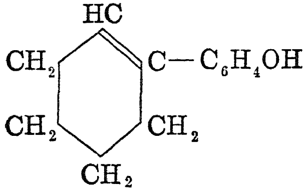
Fraction No.	Boiling Range, T., ° C.	Amount, G.	Remarks
1	75–110	22	
2	110–180	9.5	
3	180–196	50.5	
4	196–220	16.5	
5	220–280	5.5	
6	280–305	11.5	Solidified on standing
7	305–318	17.5	" " "
8	318–320	4.5	" " "
9	Residue	5	" " "

Fractions 3 and 4 dissolved completely in alkali and consisted of unchanged phenol.

Fractions 6, 7, and 8 were combined and crystallized from petroleum ether. The resulting crystals melted at 124–125° and reacted instantly with potassium permanganate solution.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 82.2; H, 8.0. Found: C, 82.0; H, 8.6.

According to these data, the reaction product was chiefly hydroxyphenylcyclohexene, in which the position of the double bond remains undetermined.



Condensation of Cyclohexanone.—It was interesting to study the condensation of cyclohexanone in the presence of phosphoric acid.

Mannich [1] studied the condensation of cyclohexanone as catalyzed by sulphuric acid in methanol solution and obtained cyclohexylidene cyclohexanone among other products.

Haller [2] obtained the same compound by the action of sodamide upon cyclohexanone. Its boiling point was found to be 272–275°.

For these experiments, 229 g. of cyclohexanone and 55 g. of 89% phosphoric acid were heated 10 hours at 120–130° at atmospheric pressure with continuous stirring. The reaction product was a light, homogeneous liquid which was freed from phosphoric acid by washing with water, dried, and finally distilled into the following fractions:

---

[1] Mannich, Ber., *40*, 153 (1907).

[2] Haller and Bauer, Compt. rend., *152*, 557 (1911).

TABLE 124

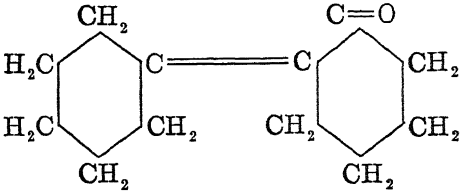
Fraction No.	Boiling Range, °C.	Amount G.
1	90–153	4.3
2	153–160	47.6
3	160–170	38.7
4	170–185	4.8
5	185–250	5.2
6	250–270	7.6
7	270–275	34.5
8	275–285	17.0
9	285–310	7.5
10	310–325	4.7
	Residue	5.0

Fractions 2 and 3 consisted of unchanged cyclohexanone.

Fractions 7 and 8 contained condensation products.

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.9; H, 10.1. Found: Fraction 7 (270–275°): C, 80.7; H, 10.3.

According to the properties and analysis of the product, cyclohexylidene cyclohexanone was the chief product of the condensation of cyclohexanone. The yield was good, based on the amount of cyclohexanone entering the reaction.



Condensation of Cyclohexanol with Phenol.—Schrauth and Görig [1] prepared cyclohexylphenol in 75% yield by heating one part of phenol with one part of cyclohexanol and one-third part of phosphorus pentoxide. The melting point of the product was 130°. They also obtained the cis- and trans-isomers of cyclohexylcyclohexanol by hydrogenation at ordinary pressure. Ipatieff and Orloff,[2] studying the hydrogenation of phenyl ether and phenol under pressure, showed that isomerization took place with the formation of cyclohexylcyclohexanol. But the properties of the alcohol obtained by Ipatieff and Orloff differed from those of the alcohol of Schrauth and Görig. Further investigation is necessary to discover the reason for these differences.

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[1] Schrauth and Görig, Ber., *56*, 1900 (1923).

[2] Ipatieff and Orloff, Compt. rend., *181*, 793 (1925).

The reaction mixture in these experiments was 0.5 molecule of cyclohexanol, 1 molecule of phenol, and ⅕ part by weight of 100% phosphoric acid. This mixture was heated 6 hours at 120–130°. Phosphoric acid (26.5 g.) separated as a lower layer. At the end of the reaction, steam distillation removed 33 g. of liquid, which after drying was redistilled into the following fractions:

TABLE 125

Fraction No.	Boiling Range, ° C.	Amount, G.
1	80– 89	8
2	89– 93	4
3	187–191	18

After distilling the second fraction, the temperature increased rapidly to 187°; the product distilling as third fraction consisted exclusively of phenol.

Fractions 1 and 2 were combined and redistilled to produce the following fractions: (1) 80–82° (8 g.); (2) 82–86° (3 g.).

The fraction boiling at 80–82° was identified as cyclohexene, since it gave all the characteristic reactions of this hydrocarbon.

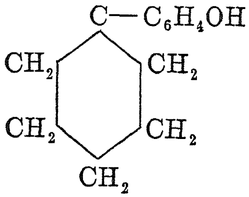
Thus there was obtained, under the specified conditions, a product whose origin was due to the dehydration of cyclohexanol under the influence of phosphoric acid. In Schrauth's experiment, the presence of this product was not confirmed.

The product remaining in the flask after steam distillation was then distilled. The fraction boiling at 210–290° solidified to a crystalline mass which on filtering and washing with petroleum ether gave white crystals melting at 126°.

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.8; H, 9.2. Found: C, 81.5; H, 9.2.

According to the properties and analysis, the product was cyclohexylphenol, presumably para.

The phenol obtained was hydrogenated under pressure in order to obtain the corresponding cyclohexylcyclohexanol.



Condensation of Acetone with Phenol.—Acetone does not condense with phenol in the presence of phosphoric acid at atmospheric pressure. But condensation takes place under pressure at 150° forming a product boiling at 280–320° which has not yet been thoroughly investigated.

Condensation of Methanol with Phenol.—The condensation of methanol with phenol was accomplished by heating at 200° for 12 hours under pressure.

In this experiment the reaction mixture was 70 g. of phenol, 35 g. of methanol, and 30 g. of phosphorus pentoxide. The reaction product was washed with water to separate the methanol from phosphoric acid and the portion which was insoluble in water was shaken with 15% sodium hydroxide solution. The liquid (24 g.) insoluble in sodium hydroxide boiled at 150–156°, n_D^{26}, 1.5730. Accordingly, it was pure *anisole.*

That part of the reaction product soluble in sodium hydroxide was pure phenol which distilled at 180° and melted at 41°.

Condensation of Ethyl Ether with Phenol.—Ethyl ether was condensed with phenol in a high pressure rotating autoclave under 30 atmospheres initial pressure of nitrogen. The apparatus, charged with 60 g. of phenol, 70 g. of ethyl ether, and 25 g. of 89% phosphoric acid, was heated at 220° for 16 hours. The reaction product was washed with water, dried with calcium chloride, and separated by distillation into the following fractions:

TABLE 126

Fraction No.	Boiling Range, ° C.	Amount
1	37– 70	30
2	70–107	3
3	107–130	14
4	130–173	28
5	173–176	18
6	176–180	8
7	180–190	5

From fraction 3, after treatment with an 18% solution of alkali, there remained 50% of an insoluble product, *phenetole*. Fractions 5, 6, and 7 consisted chiefly of phenetole formed by the action of ethyl ether upon phenol according to the equation:

$$2C_6H_5OH + C_2H_5—O—C_2H_5 \rightarrow 2C_6H_5—O—C_2H_5 + H_2O + O$$

Condensation of Acetic Acid with Ethylene.[1]—By heating 100% acetic acid with 100% phosphoric acid at 200° for 8 hours under ethylene pressure (50 atmospheres at 20°) a transparent liquid product was obtained which, after washing with water, and drying, boiled as follows: (1) 77–80° (5.5 g.); (2) 80–95° (2.0 g.). It was found that *ethyl acetate* had been produced in 10% yield.

Condensation of Acetic Acid with Propylene.[1]—By heating 60 g. of 100% acid, 67 g. of propylene, and 30 g. of 100% phosphoric acid in the high pressure apparatus at 150° for 24 hours, a transparent liquid was obtained which, after careful washing with water, was separated by distillation into the following fractions: (1) 89–93° (13.5 g.); (2) 93–95° (36.5 g.); (3) 95–103° (16.0 g.). The product was identified as *isopropylacetate* with perhaps a slight admixture of propylacetate.

[1] These experiments were made by Ipatieff and Pines.

CHAPTER X

THEORETICAL PRINCIPLES FOR CATALYTIC REACTIONS

HYDROGENATION AND DEHYDROGENATION CATALYSIS

In my[1] first article, "Pyrolysis of Organic Compounds," published in 1901, which included the results of approximately a hundred experiments, an hypothesis was postulated to explain the catalytic decomposition of alcohol. This hypothesis was based on the chemical action of catalysts and assumed the formation of intermediate compounds which could decompose under certain conditions to form the final product of the reaction with regeneration of the catalyst. Since the beginning of my experimental investigations, I have had a personal viewpoint concerning catalytic reactions which is quite different from the so-called "mechanical" hypothesis which is supported by a number of workers in the field of catalysis.

From the experimental material presented in the above-mentioned article, it is evident that there are many types of catalytic reactions. Many chemical reactions can occur in the presence of a catalyst, and also in the absence of a catalyst. To formulate a single theory covering all catalytic reactions is as impossible as it is to formulate a general explanation for all known types of chemical reactions.

Doubtless there are certain physical and chemical conditions necessary for catalytic reactions which are insignificant factors in the usual chemical processes. Later, we shall discuss the conditions necessary for a continuous catalytic reaction, but first I shall develop the hypothesis for the explanation of the dehydrogenation catalysis of the aldehyde decomposition of alcohols proposed by me more than thirty years ago. This hypothesis enabled me to predict new catalytic reactions. These predictions were confirmed not only by my own experiments, but also by those of many other investigators.

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[1] Ipatieff, Ber., *34*, 596, 3579 (1901).

After the first experiments on the catalytic decomposition of alcohols under the influence of iron, it was natural to make a comparison of the decomposition of alcohols with that of water (alcohols being distinguished from water by the substitution of a hydrocarbon radical for an atom of hydrogen, and the former, according to our conception, represents a stable grouping of atoms). If water, according to the experiments of St. Clair Deville, dissociates at 1000° without a catalyst, its decomposition might occur at a considerably lower temperature under the influence of metals (dissociation of water in an iron tube takes place at 650°). Ethyl alcohol decomposes at 750–800° in a glass tube, but in the presence of iron, decomposition starts at 450–480°. The decomposition of alcohol is a true catalytic reaction since the iron remains unchanged and the oxygen of the alcohol remains bound to the carbon atom, but in the decomposition of water, the oxygen combines with the metal forming an oxide which is not reduced to the metal; therefore, the latter reaction is not a catalytic reaction. Judging from the fact that some metals decompose water readily while others do so with difficulty, it is to be expected that not all metals will act catalytically in the decomposition of alcohols. Metals which decompose water readily are easily oxidized, and they may promote the decomposition of alcohols into aldehydes and hydrogen. Experiments confirmed this assumption.

The presence of water, although in small amounts, was always observed in the experiments on the decomposition of alcohols at high temperature, both in the presence and in the absence of catalysts. This water may have been present as moisture, or as a constituent part of the alcohol. (Water originating from the decomposition of alcohol is an unwarranted assumption.) Water in contact with metal is readily decomposed into hydrogen and oxygen, the latter combining with the metal to give metal oxide which, if easily reduced, oxidizes a molecule of alcohol to form aldehyde and water, being converted itself into metal. The water liberated in the latter reaction is again decomposed by the metal and again hydrogen as well as the metal oxide is formed which will oxidize alcohol into aldehyde, etc.

$$(1)\qquad \mathrm{Met} + H_2O \rightarrow H_2 + \mathrm{MetO}$$

$$(2)\qquad C_2H_5OH + \mathrm{MetO} \rightarrow H_2O + CH_3CHO + \mathrm{Met}$$

These equations cover the essential points. The amount of metal remains the same during the entire time that the decomposition of alcohol into aldehyde is taking place. In all probability, a part of the metal is in a finely dispersed state which is conducive to the catalytic reaction. According to these two equations, it is to be concluded that in the decomposition of alcohols into aldehydes two mechanisms are operating, oxidation and reduction. Actually, the catalytic reaction of the decomposition of alcohols is reversible, and the same catalyst may also serve for the hydrogenation of aldehydes and ketones as well as for the dehydrogenation of alcohols.

From the beginning of my investigation, I have had in mind the formulation of an hypothesis to explain the removal of hydrogen from alcohols at high temperature, this hypothesis being based on the possibility of the formation of hydrogen compounds of metals. It is likely that certain metals are able to take up hydrogen directly from alcohol at a certain temperature whereby aldehyde and the hydrogen compound of the metal are formed; the latter, however, because of its instability, decomposes into the free metal and hydrogen.

The metal hydride explanation can be applied also to the reaction of hydrogenation by means of hydrogen in the presence of reduced nickel (Sabatier and Senderens), which reaction results in the formation of cyclohexane from benzene and hydrogen. Sabatier and Senderens assumed the hypothesis of hydrogen compounds for hydrogenation catalysis and considered it contradictory to the hypothesis which I had formulated. As will be seen later, however, the hypothesis of hydrogen compounds of metals was not confirmed by the investigations of Ipatieff and others. Recent investigations of Bredig [1] show that benzene is not hydrogenated in the presence of nickel hydride (nickel saturated with hydrogen).

In my hypothesis, water is the significant factor; without it, the reaction cannot proceed. Therefore, it is obvious why the metal, which decomposes water, is also a catalyst in the decomposition of alcohol into aldehyde. The energetic course of the reaction may be explained by the fact that all intermediate products are formed *in status nascendi.*

As a test of the principle of my hypothesis, it was decided to make experiments on the catalytic decomposition of alcohols under the influence of metal oxides. A metal oxide may oxidize alcohols into aldehydes according to equation 2 and, at the same time, be reduced to metal whereby it may be obtained in a finely dispersed state; thus it may easily decompose the water separating in this reaction and again form the oxide, etc. The metal oxide may be as effective a catalyst as the metal itself.

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[1] Bredig, Z. physik. Chem., *126*, 41 (1927).

Results of experiments on the decomposition of alcohols under the influence of metal oxides are presented in Table 127.

TABLE 127

DECOMPOSITION OF ALCOHOLS IN THE PRESENCE OF METAL OXIDES

Substance	Alcohol, G.	Time, Min.	T., °C.	Catalyst	Yield of Aldehyde, G.	Yield of Gas, L.	C_nH_{2n}	Analysis of Gas			
								CO	C_nH_{2n+2}	H_2	CO_2
Ethyl Alcohol	145	60	660	ZnO	21						
Ethyl Alcohol	148	60	620	ZnO	18			3.8	3.9	91.5	
Ethyl Alcohol	140	60	600	Fe_2O_3	17			15.2	11.7	73.8	
Ethyl Alcohol	146	60	650	SnO_2	22			5.0	10.2	84.3	
Ethyl Alcohol	144	60	700	Sn (Reduced)	17			15.3	22.0	63.4	
Ethyl Alcohol	146	60	600	CuO	15						
Isobutyl Alcohol	100	70	530	ZnO	38	21.5	1.8		3.2	91.8	3.2
Isobutyl Alcohol	100	57	540	ZnO	25	22.0	0.8		3.5	94.5	1.2
Isobutyl Alcohol	100	65	590	Cr_2O_3	2	15.0	11.6	3.0	21.5	62	1.8
Isobutyl Alcohol	100	70	610	Cr_2O_3	2	24.0	20.0	13.0			1.2
Isobutyl Alcohol	100	70	530	ZnO	30	27.0	4.4	2.4	14.5	78.0	1.0
Isobutyl Alcohol	100	80	570	ZnO	44	29.0	4.0	1.2	12.6	81.4	0.8
Isobutyl Alcohol	100	65	550	SnO	26	18.5	8.4		5.4	84.0	2.4
Isobutyl Alcohol	100	60	620	SnO_2	40	14.0	12.8	3.2	12.1	65.5	6.4
Isobutyl Alcohol	100	65	420	NiO	9	24.0	12.0	6.8	34.0	47.0	0.2
Isobutyl Alcohol	100	70	450	NiO	16	23.5	11.4	2.0	29.0	56.4	0.2

Reviewing the results obtained, it is evident that the metal is a catalyst and that its oxide is also a catalyst. But the oxide may not be completely reduced to finely dispersed metal. For example, zinc oxide is not reduced to metallic zinc in any appreciable amount but it is, nevertheless, an excellent catalyst. It is possible that alternate reduction of zinc oxide and oxidation of the reduced product proceeds in the same manner as in the catalytic decomposition of alcohol by metallic zinc in which a very small amount of a white coating of zinc oxide is always formed upon the zinc.

Oxides participate in the catalytic decomposition of alcohols by metals as may be seen from experiments on the catalytic decomposition of alcohols in the presence of tin oxides. If metallic tin is placed in a glass tube and the tube is heated to 660–700°, there is no decomposition of alcohol when alcohol vapors are passed over the molten tin, but if tin oxides are placed in the glass tube and the tube heated to 650–660°, an energetic decomposition of alcohol takes place. At the beginning of the reaction, the oxide oxidizes the alcohol and is converted into dispersed metallic tin which serves as catalyst for the aldehyde decomposition of alcohol. It is interesting to note that the reduced tin which was in the form of a powder did not melt in spite of the high temperature. Analysis of the tin content (average of six analyses) after the experiments on the decomposition of alcohol indicated a tin content of 98.5%. (A certain amount of carbon was also present.) The fact that tin, being in such a finely dispersed state, did not melt induced me to believe that the minute particles of tin were coated with a very thin film of oxide and that it was the latter which was responsible for the aldehyde decomposition of the alcohol. This is readily understood in the light of my hypothesis.[1] Likewise, the fact that molten zinc, which is an effective catalyst for the decomposition of alcohols, solidified during the reaction in spite of the high temperature may also be explained by the formation of an oxide film upon its surface.

Thus, the experiments with metal oxides convinced me of the correctness of my hypothesis according to which the catalytic aldehyde decomposition of alcohol is explained by the participation of water and metal oxides. Therefore, this hypothesis was my guide in clarifying a series of facts which I had observed in the field of catalysis, and it pointed the way for further investigations and discoveries.

After the experiments on the dehydrogenation of alcohols were made and the results had been published, including the hypothesis which served as an explanation (Ber., 1901–1902), a paper by Sabatier and Senderens on the "Catalytic Decomposition of Ethyl Alcohol by Dispersed Metals" appeared in the Comptes Rendus for 1903. In this work, as well as in a series of investigations which followed, Sabatier and Senderens obtained results identical with those which I had obtained two years previously. The chief difference between their experiments and mine was that I used the metals iron, copper, etc., in a state other than one of fine dispersion; though they reacted catalytically equally well (regardless of the physical state) in the decomposition of alcohol into hydrogen and aldehyde. Secondly, the oxides which I used were converted into finely dispersed metal by reaction between the alcohol and the oxide and the resulting metal was a vigorous catalyst. I demonstrated that the metals tin and copper as such are not catalysts for the aldehyde decomposition of ethyl and isobutyl alcohols, but if their oxides are used, the finely dispersed powders formed from these oxides act as excellent catalysts.

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[1] Ipatieff, Catalytic Reactions at High Temperatures and Pressures, 1901–1907, St. Petersburg.

It is interesting to note that these predictions and observations concerning the formation of a thin film upon the surface of a catalyst were first pronounced by me in 1901 and 1902 and found their confirmation in the very interesting investigations of Langmuir who applied a very delicate physical test method to prove the presence of molecular layers of gases on the surface of solid plates.

Sabatier and Senderens, in their discussion of the two hypotheses which I proposed, namely, the participation of oxides and the formation of hydrogen compounds in the catalytic decomposition of alcohols in the presence of various catalysts, find that my first hypothesis assuming the formation of intermediate oxides is not acceptable because in their experiments with finely dispersed metals no ethylene hydrocarbons were formed. For some reason, they thought I had assumed the decomposition reaction resulting in the formation of ethylene and water as a necessary and normal reaction in the decomposition of alcohol. This idea of Sabatier and Senderens is not in accordance with the facts. I have never considered the ethylene decomposition of alcohols as a necessary antecedent for the aldehyde decomposition of alcohol. It is not at all necessary; on the contrary, all my experiments with alcohols indicate that the course of catalytic reactions depends entirely upon the chemical properties of the catalysts used. If I did state that water may appear in the aldehyde decomposition of alcohol because of a slight decomposition of alcohol into ethylene and water, it was only for the purpose of indicating this reaction as one of the reasons for the appearance of water. Again I repeat that no ethylene decomposition of alcohol is necessary; that water may be present in the form of moisture in the apparatus or in the alcohol itself, and that only a very small amount of oxide (film) is necessary in order to initiate the aldehyde decomposition of alcohols.

From the beginning, Sabatier and Senderens have not been in agreement with my hypothesis proposing the participation of oxides in hydrogenation, oxidation, and dehydrogenation catalysis. They propose to explain the hydrogenation of benzene by hydrogen in the presence of reduced nickel by means of an hypothesis involving metal hydrides. Such an idea was in my mind during the first experiments on the dehydrogenation of alcohols and, in order to decide which of these two hypotheses deserved the greater consideration, I carried out experiments on the catalytic decomposition of alcohols in the presence of metal oxides. These experiments showed that although the metal oxides were reduced only slightly, they catalyzed the hydrogenation of organic compounds with a higher velocity than did the reduced metal itself. This circumstance induced me to consider the hypothesis of metal hydrides as less probable. Recently, however, Schlenk has experimented on the preparation of hydrides of nickel, and has reported the isolation of nickel hydride, (NiH_2). Bredig's [1] experiments show that nickel hydride does not hydrogenate double bonds. I wish to say, however, that in the case of hydrogenation it is possible that in certain reactions hydrides of metals could be formed and that they might act as catalysts.

It is known that atomic hydrogen combines with unsaturated compounds in the absence of any catalyst and therefore, the possibility of the hydrogenation of organic compounds in the presence of metallic hydrides is not to be ignored. But the facts at our disposal are sufficient justification for explaining catalytic processes involving reduction and oxidation, in nature as well as in laboratory by means of metal oxide and water.

After I had published the results of my experiments on the dehydrogenation of alcohols in the presence of iron, zinc, and other metals and their oxides, Sabatier and Senderens proposed reduced copper as the best catalyst for the aldehyde decomposition of alcohols, and they stated that no ethylene hydrocarbons were formed. Such a statement contradicts my hypothesis of the participation of oxides and water in the dehydrogenation of alcohols.

To test the assertion of Sabatier and Senderens, I made a series of experiments with isobutyl alcohol in the presence of reduced copper, as well as of iron and zinc. The results obtained are presented in Table 128.

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[1] Bredig and Allolio, Zeit. physik. Chem., *126*, 41 (1927).

TABLE 128

DECOMPOSITION OF ISOBUTYL ALCOHOL IN THE PRESENCE OF IRON, ZINC, AND COPPER

Alcohol, G.	Time, Min.	T., °C.	Catalyst	Product		Gas Analysis				
				Aldehyde Obtained, G.	Gas Obtained, Liters	C_nH_{2n}	CO	C_nH_{2n+2}	H_2	CO_2
177	60	420	Cu (Reduced)	40	15.0	0.6			98.0	0.4
148	65	430	Cu (Reduced)	25	13.5	0.8			98.1	0.6
150	60	480	Cu (Reduced)	45	18.0	2.0	1.0	2.0	94.2	0.2
105	60	470	Fe (Tube)	30	25.0	5.4	4.3	4.2	86.4	1.0
100	60	450	Cu (Reduced	40	14.0	1.0		3.2	95.8	
100	60	520	Cu(Reduced)	41	16.0	1.2		1.0	97.5	0.2
100	60	560	Cu (Reduced)	38	15.0	3.6	1.0	3.0	92.4	
100	60	570	Cu (Reduced)	31	12.0	2.8	1.0	3.0	93.0	0.2
100	55	500	Fe (Tube)	25	16.0	4.8	3.6	5.6	86.1	0.2
100	50	520	Fe (Tube)	30	22.0	4.6	3.6	5.5	86.4	0.2
100	48	530	Fe (Tube)	31	21.0	5.2	2.6	6.1	86.2	0.2
100	55	550	Zn (Metal)	41	19.0	1.2		3.0	95.8	

On reviewing the data presented in Table 128, it is seen that the decomposition temperature of isobutyl alcohol in the presence of reduced copper is somewhat lower than with iron and much lower than with zinc. But it is necessary to note that very soon, due to decrease in catalytic activity, the temperature must be increased so that eventually it approaches the temperature required for zinc. In general, the decomposition of alcohol in the presence of reduced copper is similar to the decomposition of alcohol in the presence of metallic zinc or zinc oxide, but the yield of aldehyde is greater in the presence of zinc than in the presence of reduced copper.

The formation of ethylene hydrocarbons in the decomposition of alcohols in the presence of reduced copper which Sabatier and Senderens emphasized, no doubt occurs, and therefore, this objection against my hypothesis is to be ruled out. Analysis of the copper (reduced by hydrogen) before and after use in the decomposition of alcohol showed that copper is but slightly affected by the reaction. The copper content of the reduced copper did not reach 100% either before or after the experiment. The copper content of the reduced copper was 98.12% before and 98.55% after the experiment. This difference in copper content must be ascribed to oxides contained in it, the presence of which may explain the phenomenon of catalysis.

But if copper oxide is used as catalyst, an aldehydic decomposition of alcohol also takes place (as shown by my previous experiments 1) and the copper oxide is reduced to finely dispersed metallic copper. In this case, however, the decomposition proceeds with more difficulty than in the presence of previously reduced copper, and the higher temperature required for the decomposition causes the formation of a large amount of olefins. The reason for this difference lies in the fact that a high temperature is required to reduce copper from its oxide by alcohol and, in addition, copper so reduced may be poisoned by the decomposition products of the alcohol. Further experiments were made in which isobutyl alcohol vapor was passed through glass tubes [2] containing various oxides and metallic catalysts. The data obtained from these experiments are summarized in Table 129.

TABLE 129

DECOMPOSITION OF ISOBUTYL ALCOHOL IN THE PRESENCE OF METALS AND METALLIC OXIDES

EXPT. No.	ISO-BUTYL ALCOHOL, G.	TIME OF REACTION, MIN.	T., ° C.	CATALYST	PRODUCTS		GAS ANALYSIS				
					Aldehyde, G.	Gas, Liters	% C_nH_{2n}	% CO	% C_nH_{2n+2}	% H_2	% CO_2
1	100	60	720	Cr	10	16.0	33.0	5.6	39.0	20.2	0.2
2	100	65	600	Cr_2O_3		13.0	11.8	3.2	21.7	62.0	1.6
3	100	70	670	Cr_2O_3		24.0	20.4	13.4	24.4	41.0	0.4
4	100	70	700	Mn	21	13.5	7.4		15.0	78.0	
5	100	65	710	Mn	22	15.0	12.2	1.4	15.1	71.4	
6	100	70	630	MnO_3	37	20.5	5.8		23.0	71.0	0.6
7	100	60	500	Fe	30	25.0	4.8	3.6	5.5	86.4	0.2
8	100	65	420	Ni_2O_3	9	24.0	12.0	6.8	34.0	47.0	
9	100	60	520	Cu reduced	41	16.0	1.2		1.0	97.5	0.2
10	100	60	570	Cu reduced	31	12.0	2.8	1.0	3.0	93.0	0.2
11	100	100	700	Cu_2O	17	19.0	18.4	4.8	25.4	40.4	0.4
12	100	65	550	Zn	60	26.0	2.4		3.4	94.0	0.4
13	100	55	570	Zn	58	22.0	1.4		3.2	94.8	0.6
14	100	70	530	ZnO	30	27.0	4.4	2.4	14.5	78.0	1.0
15	100	80	570	ZnO	44	29.0	4.0	1.2	12.6	81.4	0.8
16	100	65	550	SnO	26	18.5	8.4		5.4	84.0	2.4
17	100	60	620	SnO_2	40	14.0	12.8	3.2	12.1	65.5	6.4
18	100	70	750	W	21	21.0	60.2		17.2	21.6	1.0
19	100	65	720	UrO_2	16	13.0	72.0		18.0	9.0	1.1
20	60	75	670	Ag	8	8.0	22.6	5.4	30.2	29.7	2.1
21	72	60	700	Ag_2O	5	8.5	25.2	7.2	30.0	35.2	2.4

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[1] Ipatieff, Ber., *34*, 3579 (1901); Ber., *35*, 152 (1902); J. Russ. Phys. Chem. Soc., *40*, 508 (1908); C.A., *3*, 1007 (1909).

[2] The temperature was measured by means of a thermocouple which was attached to the outside of the glass tube.

From a review of this table, the following conclusions may be drawn:

(1) Whenever a metal catalyzes the aldehydic decomposition of alcohol, its oxide also, in the majority of cases, possesses the same property. Thus, for example, zinc oxide cannot be reduced to metallic zinc in any appreciable amount (only traces can be detected), but nevertheless it is a good catalyst. It may be possible that lower oxides of zinc are formed with traces of metallic zinc which are intermittently oxidized and reduced and therefore effect the catalytic process.

(2) Considering the action of metals and their oxides upon alcohols, it is concluded that their catalytic properties depend to a great extent upon their position in the Periodic Table of Mendeléeff. When these metals and oxides are arranged according to increasing ability to bring about aldehyde decomposition of alcohols, the following series results: chromium, manganese, iron, cobalt, nickel, copper, and zinc. Chromium does not give good aldehydic decomposition of alcohols even at high temperature; manganese and iron are fairly good catalysts; while cobalt and nickel produce a very strong decomposition. The best catalyst for aldehyde production is zinc. Reduced copper is also very good but it quickly loses its activity.

(3) The ability of catalysts to decompose aldehydes into saturated hydrocarbons and carbon monoxide increases according to the position of the catalysts in the Periodic Table, manganese, iron, cobalt, and nickel. Thus, for example, manganese does not form carbon monoxide from aldehydes even at a high temperature, whereas nickel produces a very strong decomposition at a relatively low temperature.

For a comprehensive study of the different types of catalytic reactions, it is necessary to conduct accurate investigations using different metals and their oxides.[1] In this way the relation between the chemical and physical properties of catalysts will be established, and the reactions which they produce within the molecules of chemical compounds will be readily observed.

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[1] Table 130 on p. 213 of Sabatier's book Die Katalyse in der organischen Chemie (1927) which presents the results of experiments on the decomposition of alcohols under the influence of different oxides is not conclusive. Some data are incorrect, for example, in the case of magnesium oxide. Also, the formation of traces of hydrogen cannot be accepted as proof of the aldehyde decomposition of alcohol.

From my first investigations the following conclusions may be drawn:

(1) A given catalyst promotes only a definite reaction, i.e., it has a *selective effect.*

(2) The introduction of a catalyst markedly decreases the temperature required for the reaction.

(3) In order that a given reaction, even an isothermal one, may start, it is necessary to introduce a definite amount of heat before it will be possible for a catalyst to show its activity.

However, experiments show that the mere introduction of heat into the system is insufficient. The decomposition of an organic substance may be initiated by the introduction of a catalyst, but it may be advisable to augment its activity with the addition of a small amount of heat energy. Of course, the catalyst remains unaffected throughout the reaction.

In this way I conceived the idea of calling a catalyst a *transformer* because of its ability to convert heat energy into chemical energy which causes a decomposition reaction to proceed at a much lower temperature than otherwise possible. However, in order to clarify the mechanism of catalysis, one should not consider merely the fact that a catalyst transforms heat energy and other forms of energy into chemical energy, though this factor deserves consideration inasmuch as it enables us to apply the principles of thermodynamics to catalytic processes. Recently, actual attempts have been made in this direction which permit the drawing of valuable conclusions concerning the comparative action of various catalysts.

This idea that a catalyst is a transformer of different kinds of energy into chemical energy finds now interesting applications in the explanation of chain reactions.[1]

At the time when Sabatier and I began studying catalytic reactions of organic compounds, Ostwald [2] and Bredig [3] presented their definitions for, and interpretations of, processes involving catalysis. Ostwald considered a catalyst as a substance which accelerates a process rather than as a source of energy; i.e., a catalyst is a substance which accelerates only such processes as may proceed spontaneously even though at a very low velocity.

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[1] Semenoff, Chain Reactions, Leningrad, 1934.

[2] Ostwald, On Catalysis, Z. physik. Chem., *15*, 329 (1902).

[3] Bredig, Z. Elektrochem., *9*, 735 (1903).

TABLE 130 (OF SABATIER)

Catalysts	Gas Formed per Minute, Cc.	Analysis, % by Vol.	
		Ethylene	Hydrogen
Cr_2O_3	4.2	91	9
SiO_2	0.9	84	16
TiO_2	7.0	63	37
BeO	1.0	45	55
ZrO_2	1.0	45	55
UO_2	14	24	76
Mo_2O_5	5	23	77
Fe_2O_3	32	14	86
V_2O_3	14	9	91
ZnO	6	5	95
Dehydrogenating Catalyst			
MnO	3.5	0	100
MgO	Traces	0	100

According to this idea a catalyst interferes with the conditions of a pseudo-equilibrium.

The accelerating action of a catalyst is caused only by the removal of passive resistance from the system. Since a catalyst is not changed during the process it is not a source of energy. If a catalyst is responsible for the formation of an intermediate product, then the intermediate product cannot be a more active substance than the original; but on the other hand, due to a constant regeneration of the intermediate product, there would be no gain in energy. Bredig, sharing Ostwald's viewpoints, considered that a stoichiometrically equivalent relationship between the amount of catalyst present and the amount of product formed is not a necessary condition.

Since my first investigations in 1901 on catalytic reactions, namely, the dehydrogenation of alcohols by metals and their oxides, I have maintained still another viewpoint concerning catalysis which is contrary to that of Ostwald and Bredig. I have considered that catalysis is a type of chemical phenomenon, and that in order to understand it thoroughly it is necessary to know the chemical properties of the catalysts, and to find a reason for the course pursued by catalytic reactions in the formation of intermediate compounds with the catalyst. One cannot assume that the rôle of the catalyst is merely the removal of passive resistance from the system because various types of catalysis proceed in one direction only. Thus, for example, by careful manipulation of an experiment in an apparatus devoid of air, alcohol decomposed in the presence of alumina at 400 to 500° forming only ethylene with no trace of aldehyde. Even if it is assumed that the decomposition of alcohol into aldehyde and hydrogen proceeds with an infinitesimal velocity at ordinary temperature then, under the influence of a high temperature (500°), the velocity of this reaction should have a measurable value. However, not even the slightest trace of aldehyde was detectable at this temperature. At 500°, the molecule is close to its disintegration temperature in various directions, and if the catalyst used strongly accelerates the decomposition reaction in one direction, then why, under such favorable circumstances, does not the decomposition reaction occur in another direction, even though in small amounts?

Similarly, isobutyric aldehyde when subjected to a long period of heating at 400° under a pressure of 200 atmospheres is unable to combine with hydrogen introduced into a high pressure apparatus containing a tube of phosphor bronze; though in an apparatus equipped with an iron tube, the conversion of aldehyde into alcohol occurs rapidly and at a much lower temperature. It is known that temperature increases the reaction velocity to a great extent. If the aldehyde could combine with hydrogen very slowly at a low temperature without a catalyst, then at high temperature (400°) and under the pressure employed in the experiment, the formation of alcohol should take place, at least in small amounts. Actually, this is not the case.

Besides, I cannot consider a catalyst as a "smoothing" agent because experiments show conclusively that a chemical interaction takes place between the catalyst and a system possessing a passive resistance. Thus the aldehydic decomposition of alcohols represents an oxidation process requiring a catalyst which is able to reduce and oxidize; the ethylene decomposition of alcohol requires the catalyst alumina which is able to hydrate and dehydrate.

This viewpoint developed in my investigations on catalysis of organic compounds at high temperatures was shared in part by Traube,[1] Bach and Engler,[2] and Wieland.[3] In all processes, water plays an important part in one way or another. Thus, in the interesting work of Wieland "On the Combustion of Carbon Monoxide in the presence of Air at Ordinary Temperature with Platinum Black as Catalyst" it is indicated that the catalytic oxidation process may proceed under the influence of water. In all experiments, water served in the capacity of a true catalyst.

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[1] Traube, Ber., *15*, 659, 2121 (1888); *18*, 1877, 1890 (1891).

[2] Bach and Engler, Ber., *30*, 1669 (1897).

[3] Wieland, Ber., *45*, 680 (1912).

Data obtained from a variety of experiments involving ordinary reactions, catalytic reactions, and explosion phenomena are convincing that the interaction of components does not occur without the participation of water. Therefore, for an explanation of many of the catalytic processes, such an action must be taken into account. For example, according to my experiments nickel reduced at 300° is oxidized at ordinary temperature by moist oxygen, while dry oxygen at the same temperature has no effect. Nickel oxide which has been heated to glowing is not reduced by hydrogen under high pressure even at 250°, while nickel oxide which has not been heated to glowing is reduced completely to metallic nickel at 172°.[1] Similarly, strongly heated aluminum oxide loses the property of producing catalytic dehydration of alcohols.[2]

Since experiments lead to the conclusion that in order to understand catalytic reactions it is necessary to find a *chemism* [3] between the catalyst and the substances participating in the reaction, then it must be assumed that intermediate products form and decompose readily. Under these conditions, the catalyst will revert to its primary state and recombine repeatedly with the substance participating in the reaction. A catalytic reaction is therefore a chemical reaction for the participating components which form intermediate products with each other which exist for only an infinitesimal period of time under the conditions of the process.

The formation of these intermediate compounds follows stoichiometric laws and the catalyst repeats this reaction indefinitely. A catalyst could be called a *multiplier* of a given chemical reaction. It must also possess sufficient chemical potential to be subjected to conditions which make the multiplication of the reaction possible.

We shall take as example, a catalytic reaction in which we know that the intermediate compound can break down to regenerate the catalyst and form a reaction product. Such an example is the polymerization of propylene in the presence of phosphoric acid.

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[1] Ipatieff, The Rôle of Oxides in the Phenomenon of Catalysis, 1907.

[2] Ipatieff, Ber., *37*, 2986 (1904).

[3] Chemism is a term used in German and Russian literature which can be translated as chemical effect.

At 150° propylene does not polymerize even though heated for a very long time. In the presence of phosphoric acid, as our experiments have shown, propylene at 50–100° forms with phosphoric acid the isopropyl ester which is stable at this temperature. But, at 150° this ester decomposes and from two molecules of ester is formed the first polymer of propylene, hexylene:

$$PO(OH)_2—O—C_3H_7 + PO(OH)_2—O—C_3H_7$$

When the reaction between propylene and the acid takes place at 150°, no isopropyl phosphate is found, but only the polymers of propylene. Since the phosphoric acid is regenerated by the decomposition of the esters, it will be able to again form esters with propylene which in turn will form polymers and regenerate the catalyst. The reaction will be repeated many times before the catalyst loses its ability to form the intermediate compound. This intermediate compound is formed according to stoichiometric laws, as we see in the above example.

What is the catalyst doing? It takes part in the cycle of reactions and after each cycle is regenerated and is therefore able to repeat this cycle many times. From my point of view, the catalyst is a *multiplier* of or a *multi-actor* in a given reaction, and one can measure how many times the reaction is repeated. For instance, our experiments show that one molecule of phosphoric acid can transform 96 molecules of propylene into the polymers hexylene, nonylene, and isododecylene. It is logical to denote as "multiplier" such a substance which is able to repeat a reaction many times under the same conditions with regeneration of itself to its initial state.[1]

It is incorrect to say that a catalyst only accelerates reaction. To verify this idea it would be necessary to prove that with a catalyst the reaction is the same as without a catalyst. Evidence in disproof of such a view is found in the polymerization of ethylene under pressure, the reaction products formed in the presence of catalyst being distinctly different than those formed in the absence of catalyst.

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[1] I chose this term because it is easy to translate into other languages. It is the life of the catalyst under certain definite conditions. Theoretically, the catalyst should repeat a reaction infinitely, but in practice different causes stop its action, such as the accumulation of products of reaction, tar formation, side reactions, etc.

Polymerization of propylene is another good example of a case in which the catalyst is more than an accelerator of the reaction. In this case it is impossible to compare the speeds of reaction at 50° and 310°. The reaction (polymerization) cannot take place at the lower temperature and moreover at high temperatures the cycle of possible reactions and the resulting products are dependent upon the temperature. One may criticize the introduction of the term multiplier instead of catalyst which was introduced by Berzelius. One may also consider that heat is a multiplier since it increases the speed of reaction. But analysis of this comparison leads to the conclusion that it is fallacious. At first, addition of heat increases the amount of energy in a given reaction; this a catalyst cannot do. *A catalyst is only a transformer of energy.*

The added heat increases the speed of reaction approximately in proportion to the increase in temperature. A catalyst or multiplier of reaction repeats the reaction many times independently of the increase of temperature although temperature may change the speed of these cycles.

The number of cycles may be less if the temperature is too high although the frequency may be greater. High temperature increases the activity of a catalyst at the expense of its life. A very good instance of this is the catalytic addition of hydrogen chloride to ethylene at 80° in the presence of aluminum chloride.[1]

If we introduce the term multiplier or multi-actor we can distinguish catalytic reactions from ordinary by addition of the word *multi.* Of course, change from the term catalyst to another one presents great difficulty. But, at the same time it will be useful to introduce this term as a conception of catalysis. An advantage of this term is that it will encourage search for the intermediate cycles of catalytic reactions.

The introduction of the term multiplier or multi-actor leads logically to the conclusion that in the future it will be possible to characterize different "multipliers" quantitatively by determining their activity based on the number of cycles which they can undergo.

From the beginning of my investigations, I adopted such a viewpoint and have tried to find, in discovering new catalytic reactions, the chemical basis for the catalytic reaction.

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[1] Tulleners, Tuyn and Waterman, Rec. trav. chim., *53*, 544 (1934).

The difficulty in studying catalytic reactions lies in the fact that by our methods of investigating chemical phenomena we are unable, in the great majority of cases, to prove the existence of these intermediate reactions and the formation of unstable intermediate compounds. Recently, I studied certain catalytic reactions in which the formation of intermediate products has been proved just as definitely as the formation of esters of sulphuric acid in the preparation of ethyl ether. Further, I shall describe in detail the polymerization of olefins under the influence of phosphoric acid, as well as of other acids. If the course of a catalytic reaction with a given catalyst is definitely known, it should be possible to predict and to explain the course of an identical catalytic reaction using catalysts similar in their chemical properties to the catalyst used in the first reaction but from which we have been unable to separate the intermediate products. It would be interesting and important to classify the types of catalysts and to compare the reactions which these catalysts have induced.

A catalyst, in order to develop the maximum velocity of a chemical reaction and to multiply that reaction, must possess special chemical and physical properties. Its surface must be such as to produce maximum adsorption and reactivity because catalytic reactions are surface reactions. A certain degree of fineness and porosity is necessary to increase the surface in order to create conditions favorable for catalytic reactions. The investigations directed toward the study of adsorption upon the surface of a catalyst are very important; and it would be equally useful if the influence of the adsorptive ability of a catalyst upon the course of chemical processes and catalytic reactions were also noted.

At present, it is a known fact that adsorbents similar in physical and chemical properties do not necessarily produce the same catalytic effects and therefore, it is to be assumed that films on adsorbents have a specific behavior. It is clear that an understanding of catalytic processes must be sought in the mutual chemical action of the components participating in the reaction.

If adsorption is the explanation of the phenomenon of catalysis, it follows that a good adsorbent must also be a good catalyst, but actually this is not the case. Thus, for example, two similar substances, alumina and silica behave with marked difference in the dehydration of alcohols, though both colloids are able to adsorb almost equal quantities of water.

OXIDATION AND REDUCTION CATALYSIS

For the hydrogenation of unsaturated compounds, such as olefins and aromatic compounds, a catalyst is necessary for the activation of the hydrogen. Experiments by Ipatieff in the absence of any added catalyst show that in spite of high temperatures (above 400°), high pressures, and prolonged heating, hydrogen does not combine with isobutyl aldehyde in a tube of phosphor bronze; nor does benzene hydrogenate in an iron tube at high pressure and a temperature above 500°. The best hydrogenation catalysts are the metals which are readily produced by reduction from their oxides and which also decompose water with liberation of hydrogen *in statu nascendi.* Sabatier and Senderens pointed out that reduced nickel was an excellent catalyst in the hydrogenation of most organic compounds. Prior to the work with nickel, it was known that platinum black was able to catalyze the hydrogenation of unsaturated organic compounds containing a double bond.[1] Ipatieff's studies indicate that a metal oxide is preferable to the reduced metal in that hydrogenation proceeds with greater velocity due to the fact that water as well as the reduced metal separate *in statu nascendi.*

Depending upon the chemical potential of the intermediate reactions leading to the formation of active hydrogen, any one of the various types of hydrogenations may occur. Besides this, catalysts which bring about oxidation are also able to bring about reduction. In a series of experiments on oxidation and reduction catalyzed by iron, nickel oxide, and other substance, Ipatieff [2] showed that there is an equilibrium between alcohol, aldehyde, and hydrogen at a certain temperature and pressure. A similar equilibrium phenomenon was observed by Zelinsky [3] in the reduction of tetrahydroterephthalic ester by hydrogen in the presence of palladium black, tetrahydroterephthalic ester decomposing into hydrogen and terephthalic ester. As an explanation for this phenomenon Zelinsky cited the formation of Bach's hydrogen sub-oxide which oxidizes or reduces the initial ester. Such explanations are unnecessary, and they complicate the mechanism of the reaction, especially since the existence of hydrogen sub-oxide has not yet been proved. Assuming that the decomposition of water is only possible by a catalyst in the presence of an "acceptor" which is able to undergo reduction and knowing from experimental evidence that catalytic reactions can be reversible, the formation of the various products of this reaction is clearly understood not only in the case of metals of the platinum group, but also in the case of other metals and substances which may initiate reversible catalytic reactions. In all such cases, oxidation-reduction processes will be observed.

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[1] Wilde, Ber., *7*, 353 (1874).

[2] Ipatieff, J. Russ. Phys. Chem. Soc., *38*, 75 (1906).

[3] Zelinsky, Ber., *44*, 2305 (1911).

Such an explanation may also be applicable in oxidation-reduction catalysis of organic substances in the presence of water as accelerated by a catalyst or a ferment. This explanation may be employed in the oxidation of amino acids by aloxane, the oxidation of aldehyde by water, and the oxidation of methylene blue in the presence of palladium or Schadinger's ferment (present in milk). The difference between oxidation-reduction catalysis and ordinary catalytic reduction previously mentioned is due to the fact that there are two participating substances in oxidation-reduction catalysis, one of which is reduced by the hydrogen of the water molecule and the other is oxidized by the hydroxyl group of the water molecule; the palladium or the ferment merely accelerates this process.

Another explanation of oxidation-reduction catalysis is the participation of a catalyst which can be easily oxidized and reduced by water. This interpretation is similar to that applied to metabolism in a living organism. In an interesting article by Bach concerning this question and about which much important data have been compiled, we find a complete parallel drawn between the action of organic ferments (oxidases, peroxidases, perhydrases) and the complex acceptors which are the nuclei of the cells, and the protoplasm of a living organism possessing strong reducing properties. In order to understand the oxidizing and reducing properties of these substances, it is sufficient to assume according to Bach that the nucleus oxidizes not by means of free oxygen, but by the participation of the oxygen from water, the hydrogen of which has been transported to the surrounding protoplasm by means of the ferment-catalyst perhydrase causing the formation of strong reducing substances.

Depending upon the chemical potential of this reaction which releases the active hydrogen, the hydrogen may be applied to ordinary chemical reactions involving the reduction of organic compounds. Likewise in ordinary catalytic reactions a great difference is observed in the action of various catalysts, i.e., metals and their oxides in reduction catalysis. Thus, for example, copper oxide may hydrogenate a double bond, but it is unable to effect the addition of hydrogen to the aromatic nucleus. On the other hand, nickel, platinum, and palladium are good catalysts for hydrogenating aromatic compounds. Experiments by Willstaetter[1] on reduction catalysis of aromatic compounds in the presence of palladium black and acetic acid at ordinary temperatures show that the acetic acid increases the catalytic effectiveness of palladium to a considerable extent. Applying my explanation for oxidation-reduction catalysis, we must consider that acetic acid plays the rôle of water and that the active hydrogen separated acts very energetically.

My experiments on hydrogenation by means of metal oxides showed that only a comparatively small reduction of the metal oxides is necessary to hydrogenate organic compounds at a higher velocity than with more completely reduced metal. This fact raises the question: "To what should the catalytic action in this hydrogenation be attributed, to the reduced metal, or to its oxides?" If hydrogenation were conducted in the presence of nickel oxide and no traces of metallic nickel were evident, then the answer to the question would be in favor of nickel. If Moissan's conclusions concerning the reducibility of nickel oxide were correct, they would constitute most excellent proof that only oxides act as catalysts in reduction reactions. My experiments, however, present an entirely different picture of the ability of nickel oxide to be reduced and show that when hydrogenation takes place the formation of metallic nickel always occurs, although only in traces. Thus, the question confronting us increases in complexity and its solution becomes problematical.

In order to clarify the situation, I carried out experiments comparing the maximum velocity in the hydrogenation of benzene at 250° in the presence of nickel oxide, and at 270–280° in the presence of reduced nickel, other conditions being as far as possible the same in both cases. In all experiments, the value $(dP/dT)_{\max}$ (maximum change of pressure per unit time) for nickel oxide was considerably larger than the same value obtained for the reduced nickel.[1] Such a comparison of maximum reaction velocities favors the assumption that metal oxides play an essential rôle in reduction catalysis. If the maximum reaction velocity had been greater in the presence of reduced nickel, the hypothesis for the formation of metal hydrides would seem more probable. But now the assumptions set forth in the hydride hypothesis are being gradually discredited.

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[1] Willstaetter, Ber., *45*, 1471 (1912).

An experiment in the high pressure apparatus on the explosion of oxygen and hydrogen in the presence of nickel oxide at 160° (refer to chapter on the rôle of oxides in the phenomena of catalysis) also indicated that nickel oxide is significant catalytically in this reaction since it was reduced only to a limited extent.

In experiments on hydrogenation in the presence of nickel oxide, in spite of a temperature of 250 to 260°, the per cent of nickel was increased very little, i.e., from 74% (which was the nickel content of the original nickel oxide) to 77%. In comparing the maximum hydrogenation velocity of benzene in the presence of slightly heated green nickel oxide containing about 2% of water with the velocity of hydrogenation of benzene in the presence of nickel oxide, the velocity of the first reaction was found to be less than the velocity of the second reaction, but greater than the maximum velocity of the reaction in the presence of reduced nickel. Therefore, without doubt, nickel oxide causes more intensive hydrogenation than reduced nickel. It may be possible that in reduction by hydrogen, nickel oxides are not reduced to metallic nickel [2] and that this reaction is hampered by the formation of lower nickel oxides which function as reduced nickel.

The interesting investigations of Willstaetter on the hydrogenation of organic compounds in the presence of reduced platinum and the rôle of oxygen in activating "spent" catalysts furnish important evidence in substantiation of my hypothesis according to which the hydrogenation and dehydrogenation of organic compounds are explained by the participation of water and metal oxides.

In the objections by others to Willstaetter's theory concerning the influence of oxygen in the hydrogenation of organic compounds, it was indicated that catalysis proceeds only when oxygen is entirely eliminated from the process (the absence of oxygen can be shown by sensitive reactions), and that therefore its presence is not at all necessary. However, it must be borne in mind that reduced catalyst always contains metallic oxide and water, even though in very small amounts. Wölbling (Halle, 1926) in his monograph on hydrogenation describes various methods for hydrogenating organic compounds and cites hypotheses proposed by various investigators who attempt to explain the mechanism of the catalytic processes involved. At the end of the book [1] in the chapter discussing the theory of catalysis, the writer reviews theoretical and experimental data on reduction catalysis and concludes therefrom that in the system of a catalytic process there is, in all probability, an equilibrium between the catalyst (i.e., the metal), its oxide, and water, and the reactions occurring between them as expressed in the equations previously given.

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[1] Laffitte and Grandadam, Compt. rend., *200*, 456 (1935), showed the platinum oxides hydrogenated much better than reduced platinum.

[2] It is interesting to point out here that the nickel obtained by precipitation with dimethyl glyoxime possesses a low activity, indicating that the presence of other compounds on the surface may decrease its catalytic activity.

It is of interest to review in general the viewpoints of contemporary investigators regarding explanations of hydrogenation and dehydrogenation catalysis and to compare them with the hypotheses which I proposed in 1901. In spite of the fact that my theoretical principles of catalysis were mentioned in a series of articles published in Ber. Chem. Ges. (1901–1912) and Journ. prak. Chem. (1907), references to them are omitted in many of the writings of contemporary investigators, although their conclusions are in agreement with mine.

In the first place, it is necessary to note the investigations concerning the adsorption of various gases by the more important catalysts. Regarding this problem, the researches of Bodenstein, Taylor, and Langmuir deserve the greatest attention since they clarified a series of questions which previously had been without definite answer.

Bodenstein and Fink, who studied the oxidation of sulphur dioxide to sulphur trioxide over a platinum catalyst, found that the velocity of the reaction was proportional to $\frac{1}{\sqrt{P_{SO_3}}}$, and that the thickness of the adsorbed layer of sulphur trioxide depended on its pressure and was proportional to $\sqrt{P_{SO_3}}$. As the velocity of the reaction changed very markedly with pressure, it was assumed that the adsorbed layer may have been of considerable thickness. However, it is difficult to explain the formation of a series of successive layers of adsorbed gas. In studying the adsorption of sulphur trioxide on platinum, Fink found that the amount of adsorbed substance was so small that under the best conditions it would be sufficient only for the formation of a monomolecular film.

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[1] Wölbling, Hydrierung (Halle, 1926), p. 97.

The most interesting and convincing experiments along these lines were carried out by Langmuir who studied the adsorption of nitrogen, hydrogen, argon, and carbon dioxide upon mica, glass, and platinum, and found that the amount of substances adsorbed at the lowest temperature was such that they formed a monomolecular layer. Similar results came from an investigation on the adsorption of phosphorus, arsenic, hydrogen sulphide, carbon monoxide, and cyanogen upon platinum. The influence of water and oxygen upon the electronic emission of tungsten was also studied. It was found that the presence of a very small amount of these substances, a monomolecular layer, was sufficient to diminish one thousand-fold the number of electrons emitted. Experiments on catalyst poisoning have proved the correctness of the hypothesis for the formation of monomolecular layers. Thus, when only insignificant traces of oxygen are present on the surface of a tungsten plate, no dissociation of hydrogen takes place. The monomolecular films formed on catalysts are very stable and can only be removed by strong heating. The latest studies on adsorption by various catalysts, carried out by Taylor, Kistiakowsky, and others, lead to interesting conclusions which will have significance in explaining the phenomena of catalysis.

At the present time, it is known that for every adsorbent there exist two types of adsorption, the primary, or irreversible, and the secondary, or reversible. The primary adsorption is accompanied by considerable evolution of heat and is characterized by high activation energy; the secondary adsorption is accompanied by small heat effect and small activation energy. The velocity of primary adsorption is very small. It is assumed that from processes of adsorption with a high activation energy, data can be obtained by which the character of a catalytic reaction may be judged.

Further investigation on the adsorption of various gases on the surface of a catalyst and a determination of the heats of adsorption led many scientists to the conclusions that the surface of a catalyst, which is composed principally of minute crystals, is unequal in adsorptive value due to dissimilarity in structure of the atoms forming the crystal lattices. Perhaps it may be assumed that the less saturated atoms are at the corners of the crystal and the more saturated atoms in the facets. Also, the unsaturated atoms may possess more active electric forces, and therefore their adsorptive properties may differ.

The heat of adsorption changes with time, being much less when the surface is almost filled. The places where atoms possess the greatest freedom may give a heat of adsorption almost equal to the heat of the chemical reaction between the adsorbent and the adsorbed substance in the gas phase.

Another inference which may be drawn from investigations on adsorption is that those places on the surface of a catalyst which show greater heat of adsorption also possess greater chemical activity. Such an assumption was made by Taylor and Kistiakowsky [1] who assumed that the activation of a catalyst is influenced by the heat of adsorption and that it occurs at those places where the heat of adsorption is high. A molecule of adsorbed gas may become activated only when the heat of adsorption is sufficient to cause its dissociation. If the heat of adsorption is insufficient, activation does not occur and the heat of adsorption is liberated in the form of heat.

As a proof of unequal activity at various points on the surface of a catalyst, experiments may be cited on the poisoning of catalysts by very small amounts of material. Pease and Stewart [2] studied the influence of carbon monoxide upon the formation of ethane and showed that very small amounts of carbon monoxide which would occupy only one per cent of the surface diminishes the velocity of the reaction by 88%. Such pronounced diminution was not observed on further addition of carbon monoxide.

From a summary of the investigations on the action of catalysts in various types of reactions, it is concluded that heterogeneous catalytic reactions proceed concurrently with the formation of monomolecular layers. The adsorbed molecules may become activated at special places on the surface of a catalyst and in some cases in the body of the catalyst itself. Unsaturated atoms may be found on the surface of a catalyst and therefore places of varying activity may exist.

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[1] Taylor and Kistiakowsky, J. Am. Chem. Soc., *43*, 2055 (1921); XXXIV Hauptversammlung der Bunsen Gesellschaft, 8 May, Berlin (1929), p. 542.

[2] Pease and Stewart, J. Am. Chem. Soc., *47*, 1235 (1925).

If we considered only new conceptions: active centers, activation on a catalyst, atoms with free affinity, etc., in explanation of the existence of various types of catalytic reactions, we could not account for the activity of the catalyst itself, or predict the direction in which a catalytic reaction would proceed. Therefore, it is necessary to select a catalyst suitable for a particular investigation so that the process may proceed at the lowest temperature and with the greatest possible velocity. From this standpoint only those hypotheses relating to the action of a catalyst and of assistance in this respect will be given credence.

Langmuir's investigations led him to formulate a special theory regarding adsorption differing from all previous viewpoints. This theory proposes that an atom is retained on a surface by the atoms lying below by the same forces which bind the atoms together inside of the mass. On the surface the forces are different; they act asymmetrically, that is, the stronger field is directed towards the outside. It is also to be assumed that unsaturated atoms are present on the surface because they possess a residual affinity which is insufficient to cause them to combine with those atoms in proximity.

According to Bragg and others, it is supposed that such forces are of the same nature as the principal or residual forces of chemical affinity. These forces, according to Langmuir, are responsible for all surface phenomena: adsorption, viscosity, condensation, etc., with the same variations in intensity characteristic of the forces of chemical affinity. The atoms of molecules on sharp-edged surfaces possess greater ability for chemical reaction than atoms located on a plane surface.

It was also established that surfaces of liquids and solids are not elastic to the collision of gas molecules. Gas molecules are not repelled upon striking a surface, but they combine or condense. Their adherence is effected by a field of force emanating from the surface and their retention depends upon the surface tension. The adsorbed layer is a direct result of this condensation. When the surface forces are weak, evaporation takes place immediately after the condensation and only a small part of the surface is covered by the condensate. The adsorbed layer has a thickness of not more than one molecule and, as soon as the entire surface is covered, the forces of the surface become chemically saturated. Langmuir found in all cases of true adsorption that the condensed layer of gas molecules on solid surfaces, oil films, or liquid surfaces, is never more than one molecule. When the surface is saturated, the adsorbed layer consists of molecules uniformly distributed. The experiments of Raleigh, Marcelin, and Devoix proved the correctness of the orientation theory in the case of an oil film upon an aqueous surface. The results of Langmuir's investigations show that in monomolecular layers of fatty acids spread over the surface of water, the molecules are so situated that the carboyxl group is turned towards the surface of water since this group has more residual affinities than the hydrocarbon chains. According to Harkins,[1] the molecules of a liquid turn with their more active polar groups ($COOH, COOC_2H_5, CN$) towards the surface. Negative catalysis may be due to the fact that orientation of the adsorbed molecule does not cause a reaction. Kruyt and Van Duin [2] showed that such reactions do not take place on carbon, but the reacting substance is adsorbed. Langmuir emphasized that adsorption is essentially a chemical process.

While the forces operating in the formation of such adsorption layers do not differ from chemical forces participating in the formation of chemical compounds, chemists have not as yet formulated a nomenclature for such types of compounds. For this reason, errors have often been committed in establishing a similarity between these phenomena and typical chemical reactions because the same terminology was applied to both.

Experiments carried out by Langmuir using carbon monoxide and oxygen showed that the maximum amount of carbon monoxide and oxygen adsorbed by platinum corresponds to a monomolecular layer which cannot be removed, either by heating, or by vacuum. Forces that retain these gases in combination with platinum are perhaps the chief forces of affinity, the relation between adsorption and catalytic action being quite well established. According to Langmuir, the intensity of the chemical activity of a solid surface is dependent upon the distribution and location of the atoms forming the surface layer.

Taylor's modification of Langmuir's viewpoints on adsorption and catalysis considers the surface as consisting of atoms of different degrees of saturation with respect to the neighboring atoms of the catalyst. Assuming that an atom of nickel has four affinities, the degree of unsaturation of an atom of nickel is between one and three. In certain cases, there may be a possibility of both components of the hydrogenation reaction attacking one and the same atom of nickel. In this regard, Armstrong and Hilditch assumed that the attraction between unsaturated organic compounds and unsaturated nickel atoms may be so great as to cause the latter to be torn off instantaneously from its neighbor as soon as the catalytic action begins. Momentarily, there may exist, outside of the solid surface, a complex unsaturated nickel compound and hydrogen, the intermediate compound being converted into the product with regeneration of the nickel.

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[1] Harkins, J. Am. Chem. Soc., *39*, 354 (1917).

[2] Kruyt and Van Duin, Rec. trav. chim., *40*, 249 (1921).

All theories concerning heterogeneous catalysis agree that catalytic action occurs on the surface of the catalyst. All substances which diminish the effectiveness of the contact of reacting molecules and the catalytic surface may be termed "anti-catalytic" Faraday was the first to show that traces of fats and other substances precipitated on the surface of platinum rendered it inert and other investigators (chiefly Langmuir) have obtained interesting results in this connection. Substances which are strongly adsorbed displace other substances for which the surface has less affinity.

The emission of electrons from a tungsten wire diminishes markedly at an oxygen pressure of 10^{-9} atmospheres. Consequently, when a tungsten filament is placed in a mixture of oxygen and hydrogen at 1200° under low pressure, oxygen combines exclusively with tungsten forming tungsten oxide (WO_3) which volatilizes from the filament. As soon as all the oxygen has combined with the tungsten, the emission of electrons from the filament increases and, simultaneously, hydrogen starts to react, first disintegrating into atoms and then reacting with tungsten oxide. Langmuir concluded from this result that even at 1200° and under low pressure, tungsten is covered with a stable layer of adsorbed oxygen which tends to prevent the emission of electrons and interferes with the formation of atomic hydrogen which normally results under these conditions. As soon as all the oxygen has been consumed in the process of adsorption during which it forms a volatile oxide with tungsten, the tungsten surface again becomes normal. The action of oxygen hinders electron emission and prevents the dissociation of hydrogen similar to the poisoning of a catalyst. There is no doubt that this is due to the adsorption by which an active metal surface becomes covered with a stable film of oxygen.

A similar poisoning effect of oxygen was also observed when heating mixtures of carbon monoxide or methane with oxygen. Tungsten oxide was formed first from the metal and its formation was independent of the presence or absence of carbon monoxide or methane. In the absence of oxygen, methane was decomposed immediately under low pressure into carbon and hydrogen by a glowing filament, the carbon forming a solid solution with the metal from which it could be removed by combustion with oxygen.

Taylor and Burns [1] and Benton [2] showed that catalysis is the result of true adsorption and that by-products act as poisons if the catalyzing surface possesses a stronger affinity for the by-products than for the reacting substance. It is well known that platinum is a good catalyst for the oxidation of carbon monoxide by oxygen, but when used for the hydrogenation of ethylene, its action is poisoned by the presence of carbon monoxide. Palladium, which has a greater affinity for hydrogen than for carbon monoxide, is a good catalyst for the hydrogenation of ethylene in the presence of carbon monoxide. Likewise, it is known that carbon monoxide is a powerful poison for nickel catalysts below 180°; above this temperature nickel is a good catalyst because under these conditions carbon monoxide and nickel have no affinity for each other.[3] Maxted,[4] on the ground of his investigations, assumed that the poisoning of a catalyst is caused by a change in adsorption. But the coefficient of diminution in the activity of a catalyst and the coefficient of adsorption are unequal. Maxted explains this situation by assuming that the catalytic activity of palladium is limited by the amount of metal surface, and that the adsorption of hydrogen does not take place. However, one must take cognizance of the fact that catalytic activity changes, depending on the method used in the preparation of a catalyst, while adsorption does not change to the same extent.

[1] Taylor and Burns, J. Am. Chem. Soc., *43*, 1272 (1921); *45*, 920 (1923).

[2] Benton, J. Am. Chem. Soc., *45*, 45 (1923).

[3] Stanley J. Greene, Industrial Catalysis, p. 89 (1928). This remark is not applicable when pressure is used, in which case the formation of nickel carbonyl is always detected.

[4] Maxted, J. Am. Chem. Soc. (1919, 1920, 1921).

ACTIVATION

Many investigators endeavor to explain the activation of reacting molecules during catalysis on the basis of intermediate compounds and adsorption. By the activation of molecules is understood an increase of their internal energy. The activation of molecules takes place either by the addition of energy or under the influence of a substance introduced into the sphere of the reaction. If we accept Langmuir's viewpoint concerning oriented adsorption, many possibilities, as indicated by Bancroft, will develop. From this standpoint, for example, all molecules turn in one and the same direction, that is, all molecules are so directed that each molecular collision occurs between the reacting groups, leading to positive catalysis. If the orientation adsorption is opposite to that occurring between the reacting molecules in a positive catalysis, then negative catalysis results.

According to this idea, activation consists in molecular rearrangement to positions favorable to reaction. An old idea expressed by Loew ascribed catalytic action to the unevennesses of a catalytic surface, which split molecules into atoms thereby activating them. Bodenstein suggested that when molecules of hydrogen are adsorbed upon the surface of a platinum catalyst they are deformed and perhaps split into atoms which are retained on the surface by electric forces acting between free atoms and atoms of the metal. Raschig [1] assumes that special forces of the adsorbed surface change the shape of the adsorbed molecules (either a splitting of the molecules into atoms, or a displacement of parts of molecules without actual splitting) whereby an increase in potential energy may occur. In this sense temperature and light may be considered as catalysts.

Arrhenius [2] was the first to explain the course of a reaction by assuming the existence of "active" and "inactive" molecules, the active molecules possessing higher internal energy than the average energy of the system. Dhar [3] showed that if active and inactive molecules participate in the equilibrium, and light, temperature, and catalyst increase the velocity of the reaction by simple displacement of this equilibrium, then the temperature-coefficient must be less, the greater the activity of the catalyst.

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[1] Raschig, Z. angew. Chem., *19*, 1748, 2083 (1906).
[2] Arrhenius, Z. physik. Chem., *4*, 226 (1889).
[3] Dhar, J. Chem. Soc., *111*, 746 (1911).

On the contrary, in the case of negative catalysis, an increase in the temperature-coefficient of the reaction should be expected. This assumption was verified for certain reactions such as the oxidation of quinine sulphate by chromic acid and the oxidation of potassium tartrate by mercuric chloride.

Mention may also be made of the "radiation" hypothesis proposed by W. C. McLewis in 1914 and by Perrin in 1919. McLewis was the first to suggest the possibility of a catalyst influencing a reaction by displacement of the equilibrium between active and inactive molecules in the manner proposed by Arrhenius, but McLewis' theory was abandoned when it was found that the temperature-coefficient in the hydrolysis of methyl acetate did not decrease with increase in catalyst concentration. Lewis then developed a theory in which it was assumed that molecules become activated by infra-red rays, these radiations emitting heat which is transmitted to a given system or which promotes vibration of a part of the molecules of the catalyst. The addition of a catalyst, or increase in temperature leads to a greater radiation in the infra-red region and the molecules absorbing these radiations are activated due to increase in internal energy. Lewis was successful in his theory by means of mathematical analysis. The theory of radiation finds ready application to catalysis in homogeneous systems but not in heterogeneous systems.

These are the generalities contributed by many investigators working toward an explanation of the mechanism of catalysis. From this, it may be concluded that for the last two decades the chief interest in the investigation of catalytic reactions was directed to its mechanical phase, the mechanism of catalysis remaining without the necessary explanation. Attempts have been made to explain them in terms of the electronic theory, by a special structure of the surface of a catalyst, or by a change in the internal energy of the system due to the presence of a catalyst.

With due regard for the significance of other investigations in catalysis and with no desire to criticize these works, there will be presented here only a few experiments which best serve the author's needs as evidence for his conception of catalysis, namely, the simple application of Ipatieff's theory of hydrogenation and dehydrogenation catalysis based on chemical reactions.

In the works of Vaughan and Lazier,[1] it is pointed out that pure zinc oxide is unable to hydrogenate ethylene at ordinary pressure, but is able to dehydrogenate alcohols with the formation of aldehyde. It is able to hydrogenate the double bond only after reduction with hydrogen. It is to be regretted that these investigators were unfamiliar with my work and with my theory, on the basis of which it could have been predicted that zinc oxide, when not subjected to the reducing action of hydrogen, would not hydrogenate the double bond, for it is necessary that the thinnest layer possible of reduced zinc or lower zinc oxides be formed in order to initiate hydrogenation in catalytic processes.

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[1] Vaughan and Lazier, J. Am. Chem. Soc., *53*, 3719 (1931). The authors do not

In the dehydrogenation of alcohol at 520–550° by zinc oxide, I was able to show that a small amount of metallic zinc is always present in the zinc oxide. The zinc also became covered with a thin layer of zinc oxides during catalysis, and the melted zinc started to solidify during the catalytic process. All these experiments, using metal oxides, were made prior to the appearance of the publications of Sabatier and Senderens.

Another point of view which merits attention concerns attempts by H. Taylor to explain the action of dehydrogenation and dehydration catalysts. This is based upon his interesting hypothesis proposed as an explanation for the different types of catalytic action by the dualistic theory of the ionic lattice of the surface of the catalyst. According to his publications on the influence of adsorption and of the action of poisons on catalysts, Taylor is an ardent advocate of unequal catalytic activity on the surface of the catalyst. To justify his support of this theory, he presented the following points:

(1) The different adsorptive capacities of a given catalyst for various gases.

(2) The relationships between the adsorptive capacities for two gases on two different samples of one and the same catalyst.

(3) The relationships of the adsorptive capacities of one and the same catalyst before and after ignition or poisoning.

In his theory on heterogeneous catalysis explaining why "a given catalyst accelerates a definite reaction only," Taylor [1] assumes that some atoms, more than neighboring atoms in the metallic

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mention the investigations (1901) of Ipatieff with zinc and zinc oxide, nor his work with Balatchinsky, Ber., *44*, 3459 (1911). Zinc and zinc oxide catalysts were first discovered by Ipatieff who used them in the aldehyde decomposition of alcohols in 1901.

[1] Taylor, Z. Elektrochem., *35*, 542 (1929).

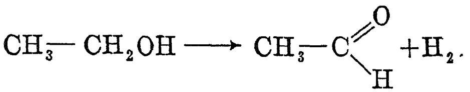
surface, may have a higher or a lower saturation valency, but never a complete one. This saturation varies from only slightly less than that inside of the crystal to a degree where atoms are retained upon the surface by one bond only.

Such a conception concerning the unsaturation of atoms gives the writer an opportunity to explain poisoning and the influence of high temperature upon a catalyst and, in general, its catalytic activity. According to the viewpoints of Taylor, all atoms in the crystal lattice have some catalytic activity.

If instead of a metallic catalyst, a metal oxide or halide, or sulphate is used, we may consider their ionic lattice as a double catalyst consisting of metallic ions and negative ions and to each of these ions a definite catalytic activity may be ascribed.

A review of the data on the action of oxidation catalysts shows that both hydrogenation and dehydrogenation are due to metallic ions, while acid ions promote hydration and dehydration. For a given substance, the relative reaction velocities of the opposing processes will be determined by the relative adsorption of the substance by both ions, by the relative number of the two ions on the surface, and by their relative activities. Upon all these factors, of course, will be superimposed the effects of unsaturation and poisoning.

On the basis of this theory, Taylor attempted to explain why the two catalytic processes of dehydrogenation and dehydration of alcohols are catalyzed by the action of tungstic oxide (WoO_3) and zinc oxide, respectively:



$$CH_3-CH_2OH \longrightarrow CH_3-C\overset{\displaystyle O}{\underset{\displaystyle H}{\lessgtr}} + H_2.$$

$$CH_3-CH_2OH \longrightarrow C_2H_4 + H_2O$$

The investigations of Taylor and his co-workers have yielded many valuable conclusions concerning adsorption and its significance in catalysis, but the writer is dissatisfied with this theory as an explanation for these catalytic reactions.

Concerning Taylor's explanations of his results on the action of pure zinc oxide, and of zinc oxide poisoned by zinc sulphate, zinc phosphate, and zinc pyrophosphate which confirm his dualistic theory of the ionic lattice, the writer finds it necessary to make some objections. The author's investigations on the catalytic action of metallic oxides gave the answer to Taylor's query: "Why does a given catalyst influence a particular reaction and not all reactions?"

At the same time the author showed that zinc and zinc oxide were excellent catalysts for the aldehyde decomposition of alcohols (ethyl and isobutyl). It is evident from the gas analyses (Tables 127, 128, 129) that only an insignificant quantity of ethylene is formed at the temperatures most favorable for the aldehyde decomposition though at higher temperatures isobutyl aldehyde may be decomposed into ethylene hydrocarbons. This slight ethylene decomposition may be explained by the chemical properties of the catalyst.

Metal oxides have the ability to combine with water to form various hydrates, this property varying in degree from oxide to oxide. Alumina, thorium oxide, and tungsten oxides possess this property to a high degree. At certain temperatures they readily remove water from other compounds, subsequently dissociating with elimination of water and returning to their original state; in other words, they are typical catalysts. Zinc oxide possesses this ability only to a limited extent, and therefore, the amount of ethylene decomposition with this catalyst is very slight. With more strongly dehydrating catalysts such as chromium oxide (Tables 127, 128, 129) the two reactions may take place simultaneously, resulting in a mixed product.

It is unnecessary to make experiments to ascertain whether the addition of such substances as sulphates or phosphates to zinc oxide will increase the yield of ethylene. They, themselves, may be catalysts in the dehydration of alcohols and, therefore, are comparatively more active for this type of reaction than is zinc oxide.

The theoretical conceptions proposed by Taylor as an explanation for heterogeneous catalysis and also the theories based on contemporary knowledge regarding the structure of atoms, crystal lattice, and adsorption are insufficient for the prediction of the activity of any given catalyst. In the opinion of the author, it is the chemical properties that must be considered in order to select a catalyst for a given reaction. For an explanation of a catalytic process, it is necessary to study chemically all the reactions that may occur in a given case and then, only, may conclusions be drawn. Otherwise incorrect conclusions may result.

From the beginning of my investigations, I noticed that some catalysts bring about decomposition of organic compounds in several directions, while other catalysts produce decomposition in only one direction. In discussing these various reactions, it is necessary to emphasize the effect of temperature and to compare the action of various catalysts at the same temperature. As an example of a catalyst incorrectly classified, mention may be made of magnesium oxide which Sabatier [1] listed as one producing the aldehyde decomposition of alcohol. According to my explanation of oxidation and reduction catalysis, magnesium oxide cannot be a catalyst for the aldehyde decomposition, since its oxide is reduced with difficulty. Nevertheless, Sabatier as well as Taylor and others, consider magnesium oxide as a dehydrogenation catalyst because at 360° it liberates traces of hydrogen. In checking the decomposition of ethyl alcohol in the presence of magnesium oxide, it was found that the decomposition of alcohol begins above this temperature and that the gases contain not more than 40% of hydrogen, and large amounts of ethylene and other gases.

A detailed description of my experiments will be presented later, but at present it is sufficient to say that even the liberation of hydrogen is no proof that aldehyde decomposition has taken place. My method [2] for obtaining butadiene from ethyl alcohol by the action of powdered aluminum shows that there is a third decomposition of ethyl alcohol,

$$\begin{array}{l} CH_3{-}CH_2OH \quad CH_3{-}CH_2OH \\ \qquad\qquad\qquad \rightarrow H_2O \quad CH_2{=}CH{-}CH{=} \qquad\quad H_2 \end{array}$$

which is accompanied by liberation of hydrogen. Thus, the presence of hydrogen in the exit gas is not sufficient evidence for deciding the type of decomposition taking place in the presence of a given catalyst; it is necessary to have complete data in order to draw final conclusions.[3] As proof of the correctness of my view as to the necessity of studying the chemical properties of catalysts most carefully in order to predict their effect, mention may be made of Maxted's[1] data contained in his report presented at the Joint Meeting of the London Section of Chemical Engineers and the Faraday Society. Maxted's viewpoints are especially interesting. In his report there is presented a proof of my conception regarding the catalyst as a *transformer of energy.* Although Maxted does not use the same words, yet the hypothesis which he proposes as explanation for catalytic processes, and his final conclusions, agree in all details with the ideas which I proposed years ago. Maxted says: "In order that a molecule of A may undergo a chemical transformation into a second molecular species B, it must possess in general also a certain minimum amount of energy, the so-called critical energy of the reaction.

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[1] Sabatier, "Catalysis," Leipzig, 1927, refer to p. 213. "Magnesium oxide is a dehydrogenation catalyst giving pure hydrogen." However, Sabatier indicates that magnesium oxide decomposes only "traces" of alcohol at 350°.

[2] Ipatieff, J. prakt. Chem., 67, 420 (1903).

[3] Perhaps a given decomposition of alcohol, e.g., aldehyde, should be classified as catalytic only when it takes place at a considerably lower temperature in the presence of a catalyst and when the yield of product, e.g., aldehyde, is more or less quantitative with respect to the alcohol decomposed.

"Normally, the critical energy of a reaction is considerably higher than the average energy, and the additional energy which a molecule of A must acquire in order to react, is known as the activation energy. The introduction of a catalyst into a chemical system which is potentially reactive brings about an increase of reactivity and, in many cases, apparently initiates a reaction velocity similar to that which would be caused by a transitory elevation of the reacting molecules to an abnormally high energy level. Accordingly, it seems pertinent to inquire whether it is possible on an energetic and especially on a *thermodynamic basis, to render available transitorily the additional energy required for the activation of a system catalyzed by the introduction of a catalyst.*

"The word *transitorily* is of considerable significance, since the addition of a catalyst causes no change in the total energy of a system; and the cycle by means of which the energy of activation becomes available must be one which is actually known to take place and one which does not conflict with the second law of thermodynamics."

The italic sentence expresses the principle of the transformation of energy, which must, of course, be "transitory" because the catalyst does not introduce additional energy into the system. The higher the activation energy of the system, or the higher the internal energy of the molecules, the more intensively is the process accelerated by the catalyst.

As an explanation of catalysis, Maxted also considers the formation of unstable chemical compounds between the catalyst and the reacting substances which are formed on account of the chemical affinity of the catalyst towards one of the reactants. He indicates as the chief condition of catalysis that these intermediate compounds should be unstable.

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[1] Maxted, Chemistry and Industry, *50*, 149 (1931).

Maxted also attempted to find reasons for the various actions of different catalysts in their chemical properties. In this respect, he sanctions our explanations as to why certain metals promote the dehydrogenation of alcohols, whereas alumina causes dehydration with formation of olefins. Maxted's discussion regarding the heats of adsorption of various metallic catalysts, activation energies, and their catalytic action will be passed over since these factors have previously been given recognition, but mention will be made of his data by which he calculated the probable contribution of free gas molecules to the required critical energy.

We quote: "Since a reaction, such as the union of ethylene and hydrogen does not take place at all, at any rate, at low temperatures in the absence of a catalyst, the energy of activation of homogeneous reactions must be very high. If for the catalytic reaction, E is of the order of 15,000 calories, it can be shown that even if the gas complies with the simple exponential energy distribution law, only one molecule in 1×10^8 has a probability of possessing energy of this order at 137°. Rideal has shown experimentally that at this temperature for the interaction of hydrogen and ethylene on nickel, about one collision in 2500 leads to the reaction. Thus, by far the greater part of the energy of activation must be supplied from a source other than the kinetic energy of gas molecules. Therefore, by plotting the results of Adkins and Perkins for the dehydration of ethyl alcohol over alumina, the conventional heat of activation is seen to be of the order to 20,000 calories. The heat of hydration of alumina for the hydroxide is of the order to 70,000 calories per gram molecule of water so that here again the transitory energy requirements are covered, etc." [1]

A catalyst may initiate a reaction only when it has an affinity towards one of the reacting substances and when a complex compound is formed which produces an active kinetic equilibrium.

Maxted stated further: "The energy of the formation or decomposition of this association complex must be at least as great as the activation energy of the reaction along its catalyzed path. This is nothing but an old intermediate compound theory modernized by what, for the time being, must be considered merely a tentative introduction of energy relationships" (energy affinity).

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[1] Maxted, J. Soc. Chem. Ind., *2*, 107 (1883).

At the end of his declaration, Maxted cites the words of Hurter: "Heat (for the decomposition of hydrochloric acid) cannot be supplied directly, except in a very few instances, known as processes of dissociation. We can easily convert potential chemical energy into heat, but only in a few instances can we convert heat into potential chemical energy."

The viewpoints concerning the essentials of catalytic processes expressed by Maxted are completely in agreement with those fundamental ideas which I had proposed at the very beginning of my investigations as being necessary for the understanding of catalytic reactions and the prediction of new catalysts.

If we endeavor to evaluate the significance of the scientific investigations made during the last thirty years in an attempt to explain catalytic reactions, we must conclude that all of the scientifically valid material at our disposal concerns chiefly a study of the physico-chemical conditions of catalysis and an explanation of the catalytic processes from a physico-mechanical point of view. Many investigators have adapted and applied the modern theories and physical methods (X-ray, spectroscopy, theory of adsorption, electronic and ionic theories, etc.) to the study of catalytic processes, enriching this field of chemistry with important contributions and giving to science and industry valuable guides for research and practice.

But we must acknowledge very little work has been done in the clarification of the chemical mechanism of catalytic reactions. If at the present time the majority of chemists and physical chemists are inclined to think that in catalytic reactions the catalyst forms unstable compounds with substances participating in the reaction, then we chemists should consider seriously the formation of such intermediate compounds. This is a very difficult problem the solution of which is not readily attained; therefore, new methods must be developed for the investigation and observation of the formation of such unstable compounds, the life of which is of the magnitude of thousandths of a second.

The excellent experiments of Langmuir showed that a monomolecular layer forms on the surface of tungsten in the presence of a mixture of hydrogen and oxygen at low pressure. At 1200°, an oxidation of tungsten takes place with the formation of atomic hydrogen and resultant reduction of the volatile tungsten oxide. This, and similar reactions studied by Langmuir are not entirely catalytic in nature, at least not in the same sense in which we would characterize catalytic reactions; nevertheless, they do add impetus to the study of catalysis. By applying a method similar to Langmuir's, under certain conditions of temperature and pressure and chemical properties of the catalyst, it would perhaps be possible to determine the presence of intermediate products, regulate conditions for their formation, and measure their rate of decomposition. In the following chapters discussing the theory of catalysis, an attempt will be made to show how the study of the formation of intermediate products between catalyst and substance leads immediately to a clarification and unification of a series of processes which hitherto have been more or less isolated with no apparent correlation between them.

If, however, we employ the hypothesis of active centers upon the surface of catalysts for an explanation of catalytic processes or the theory of adsorption (if it is not identified with chemical affinity), we will still not understand why certain substances act as catalysts, while others very similar to them in physical properties are unable to catalyze a given reaction.

The same is true for the radiation theory of McLewis, which assumes that by radiation in the infra-red region quanta of radiated energy are transmitted to the molecules of the catalyst, and to the substances participating in the reaction; therefore, they become more active because of increase in their internal chemical energy. Actually, this theory of McLewis substantiates the theory of the transformation of energy but, from a chemical viewpoint, it only partially explains the action of a catalyst. My personal conviction is that the theory of McLewis deserves considerable attention. The ideas contained in his theory are in agreement with my proposals regarding the transformation of energy in catalytic processes.

In conclusion, it may be relevant to mention the work of Le Blanc and Sachse [1] and Le Blanc and Möbius [2] in their study of the system nickel oxide, oxygen, and water. These investigators proved that an oxide higher than nickel oxide (NiO) does not exist, either in a dry or in a moist atmosphere. In 1908, I [3] demonstrated that nickel oxide is not oxidized to higher oxides, which was contrary to Moissan's experimental evidence. On the other hand, in collaboration with Konduirew,[1] it was shown that the oxide liberated from solutions of nickel salts was NiO and that Ni_2O_3 was never obtained. This is contrary to the behavior of cobalt salts in which case Co_2O_3 is obtained. Thus the work of Le Blanc and his co-workers confirms my assertions concerning nickel oxide. Additional evidence for my hypothesis on hydrogenation by nickel oxide was furnished by the X-ray observations of Le Blanc and Möbius which showed that nickel oxide contains nickel hydroxide [$Ni(OH)_2$].

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[1] Le Blanc and Sachse, Z. Elektrochem., *32*, 58 (1926).

[2] Le Blanc and Möbius, Z. Elektrochem., *39*, 753 (1933).

[3] Ipatieff, "Reduction and Oxidation of Nickel Oxide at Ordinary and High Pressure," J. prakt. Chem., 77, 513 (1908).

New work by Polanyi and Horinti[2] especially confirms the hypothesis of oxides: "In the presence of platinum or nickel there is an exchange of hydrogen atoms between gaseous hydrogen and water. When ethylene is hydrogenated on a nickel catalyst there is an exchange of hydrogen atoms between the ethylene and the hydrogen used. Metallic catalysts effect rapid exchange of hydrogen atoms between benzene and gaseous hydrogen at ordinary temperature while hydrogenation proceeds very slowly at the same time. This is a hitherto unknown reaction, resulting from the combination of the two exchange reactions mentioned above. To make the tests, ethylene or benzene and water containing 3 per cent of heavy water were heated in a closed vessel in the presence of metallic nickel for some hours. After 7 hours at 70° C. the ethylene contained 0.6 per cent of heavy hydrogen and after 24 hours an equilibrium was reached with 1.3 per cent of deuterium in the hydrogen of the ethylene. The distribution coefficient, that is, the proportion of heavy water to heavy ethylene, is 1 : 0.58 or 1.7. The corresponding value for the equilibrium between water and benzol at 200° is 1.05."

A good confirmation of my hypothesis is given also by the investigation of Laffitte and Grandadam on the oxides of platinum.[3] These authors studied the catalytic action of PtO and PtO_2 for the hydrogenation of organic substances, containing the double bonds $>C=C<$ and $>C=O$. These oxides of platinum proved to be very good catalysts for the hydrogenation of double bonds and it was found that PtO_2 is twice or thrice more active than ordinary black platinum.

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[1] Ipatieff and Konduirew, Ber., *59*, 1421 (1926).

[2] Polanyi and Horinti, Nature, London, *134*, 377, 847 (1934).

[3] Laffitte and Grandadam, Compt. rend., *200*, 456 (1935).

The great majority of the investigators in catalysis speak favorably of the formation of intermediate compounds between the catalyst and the reacting bodies. Frankenburger,[1] in his recent work on "The Chemistry of Catalysis," concludes that for an understanding of the catalysis concerned in the formation of ammonia it is necessary to think in terms of the formation of intermediate compounds between the catalyst, nitrogen and hydrogen, the decomposition of which leads to the formation of active nitrogen and hydrogen which unite to form ammonia.

$$M_xN + H \rightleftarrows M_xNH + H_2 \rightleftarrows M_xNH_3 \rightleftarrows M_x + NH_3$$

The recent work of Frankenburger and Holder[2] shows that "activated adsorption" does not furnish sufficient basis to explain catalysis. With careful exclusion of oxygen, it was found that the adsorption curves were not of the type characteristic of "activated adsorption." Polanyi[3] concludes that adsorption is not a necessary condition for catalysis and that strong adsorption does not favor catalytic activity.

Thus, one must conclude that only through a study of the chemical properties of the catalyst and of the reactions which the catalyst undergoes with the substances present in the system, can one understand catalysis and be able to predict new catalytic reactions. The X-ray method, the ionic and electronic theories, the transformation of radiated quanta of energy, and other physical theories will, of course, be of great service in the profound study of the course of catalytic process.

Exact physical methods are applicable only after the chemistry of a given process is understood, and when these methods have been applied to a study of ordinary chemical reactions, data will be obtained which can be applied to more sensitive reactions which take place at enormous speeds comparable with those encountered in catalytic reactions.

THE JOINT ACTION OF CATALYSTS; PROMOTERS

It had long been known in the literature that small amounts of certain substances influence the course of certain chemical reactions to a considerable extent, i.e., by changing its reaction velocity and decreasing the temperature necessary to start reaction. Because of the limited knowledge of the action of catalysts, these isolated facts received little consideration, especially in regard to explanation, from the scientific and the industrial world.

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[1] Frankenburger, Z. Elektrochem., *39*, 45, 97 (1933).

[2] Frankenburger and Holder, Naturwissenschaften, *23*, 609 (1935).

[3] Polanyi, J. Soc. Chem. Ind., *54*, 123 (1935).

There can be no doubt that my experiments in 1909 showed that the walls of the vessel can have a profound influence on the course of a reaction. I was studying the hydrogenation of amylene under high pressure with copper oxide as catalyst, using as apparatus the Ipatieff high pressure bomb. The experimental findings were published in the Berichte der Deut. Chem. Ges. of 1910. It was shown that the reaction was slow in a copper tube but much faster in an iron tube, though the added catalyst was copper oxide in both cases.

This finding aroused the attention of chemists and especially of Professor Paal who gave prominence to this discovery in the following number of the Berichte and used this knowledge in his investigations of the hydrogenation of organic compounds. This fact had not been previously noted, either in the chemical or patent literature. This discovery was of interest inasmuch as a hydrogenation reaction, under high pressure and temperature, was accelerated by the introduction of an active substance, which was not finely divided. Without doubt,[1] this discovery gave, not only to myself, but also to other investigators, impetus for a many-sided study of the joint action of catalysts under various conditions and for various reactions.

In 1911 and 1912, Matov and I [2] studied the reaction involved in the hydrogenation of terpenes by the joint action of nickel oxide and alumina. Alumina, alone, apparently had no effect on the hydrogenation of terpenes, but it was deliberately chosen as part of my scheme for arriving at an explanation of the course of reduction and oxidation catalysis mentioned in my investigations since 1901 and particularly those appearing in 1907 under the title, "The Rôle of Oxides in the Phenomena of Catalysis." We found that the hydrogenation of camphor, borneol, and fenchone in the presence of nickel oxide does not begin until 360–400° and proceeds very slowly with the formation of by-products. But if alumina is added to nickel oxide, the hydrogenation proceeds readily at

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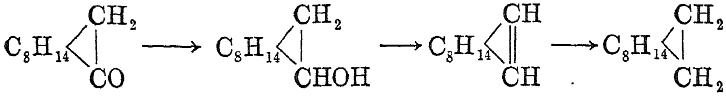
[1] Taylor and Russell, Catalytic Process in Applied Chemistry, p. 33. So far as laboratory actions are concerned Ipatieff had published observations prior to the Badishe Work.

[2] Ipatieff and Matov, J. Russ. Phys. Chem. Soc., *44*, 1695 (1912); C.A., *7*, 1170 (1913).

190–200°, producing almost a quantitative yield of crystalline camphane, fenchane, and other compounds.



$$C_8H_{14}\left<\begin{matrix}CH_2\\|\\CO\end{matrix}\right. \longrightarrow C_8H_{14}\left<\begin{matrix}CH_2\\|\\CHOH\end{matrix}\right. \longrightarrow C_8H_{14}\left<\begin{matrix}CH\\\|\\CH\end{matrix}\right. \longrightarrow C_8H_{14}\left<\begin{matrix}CH_2\\|\\CH_2\end{matrix}\right.$$

Thus, at 190–200°, or perhaps even lower, by the joint action of two catalysts (nickel oxide as reducing catalyst and alumina as hydrolytic catalyst) a very energetic hydrogenation takes place, cyclic ketones being converted immediately into cyclic hydrocarbons.

A similar reaction takes place with borneol, hydrogen acting upon it at 200° in the presence of the two catalysts nickel oxide and alumina to produce crystalline isocamphane.

But, if instead of nickel oxide, a weaker catalyst such as copper oxide is used with alumina, the action of hydrogen upon alcohols is different. In spite of the ability of copper oxide to serve as catalyst for the hydrogenation of the double bond we do not obtain saturated bicyclic hydrocarbon from borneol or isoborneol, though we do observe the formation of the unsaturated hydrocarbon camphene. Depending upon the temperature, the product is a liquid or a mixture of a liquid and a solid hydrocarbon.

In my experiments on the joint action of catalysts, varying amounts of other catalysts were added to the principal catalyst, depending upon the character of the process studied. At the end of 1910, the Badische Anilin und Soda Fabrik patented a whole series of admixtures proposed as catalysts in the synthesis of ammonia from nitrogen and hydrogen, and they named the added substance "a promoter."

Of course, it is difficult in many cases to explain the difference between the action of promoters and of mixed catalysts; and if a difference does exist, it is entirely conditional. In the hydrogenation of camphor to isocamphene it is inferred that the first step is the conversion of ketone into alcohol, which is followed by dehydration under the influence of alumina, and finally by hydrogenation of the camphene.

It is interesting to discuss here the work of Medforth, who studied in detail the hydrogenation of carbon monoxide and carbon dioxide to methanol under the influence of metallic nickel in the presence of promoters. The oxides of cerium, thorium, chromium, beryllium, aluminum, molybdenum, and vanadium act as promoters, increasing the velocity of the reaction seventeen to twenty times. They differ greatly among themselves in their intensity of action. To explain the action of promoters, Medforth assumes that complex or intermediate compounds of the type of methanol or formaldehyde are formed between the gas and the nickel. The promoters act as catalytic dehydrating agents upon the intermediate compounds, giving water and the methylene radical; therefore, methane is formed immediately, as illustrated by the following equations:

$$CO + 2H_2 \rightarrow H_3COH \rightarrow CH_2 + H_2O$$

$$CH_2 + H_2 \rightarrow CH_4$$

To prove the correctness of his dehydration hypothesis, Medforth presents certain cases illustrating the action of promoters and also the following classification of the functions of promoters.

(1) The promoter decomposes the intermediate compound formed by the catalyst.

(2) The promoter absorbed by a catalyst combines with one of the reacting substances producing a high concentration of the latter upon the surface of the catalyst.

Contrary to the conclusions of Medforth, Armstrong and Hilditch [1] ascribe the acceleration of hydrogen addition to unsaturated chains in the presence of nickel catalysts promoted by alumina, silica, or iron, to increase in the active surface of the catalyst. They explain in similar manner the increase in activity of nickel catalysts promoted by metallic copper. In short, Medforth ascribes a specific dehydrating action to the promoter, whereas Armstrong and Hilditch assume that a promoter increases the active surface of the catalyst.

Russell and Taylor [2] reported an interesting investigation on the action of thorium oxide and nickel supported on pumice in catalyzing the reaction between carbon dioxide and hydrogen to form methane and water. The reaction velocities and the gas adsorption were measured. The experimental data showed that no definite ratio exists between increase in adsorption and increase in the activity of catalysts activated by promoters. Thus, it may be inferred that the surface of the catalyst had experienced a qualitative rather than a quantitative change. Taylor found that a 0.5% concentration of cerium in a nickel catalyst causes a ten-fold increase in the velocity of the reaction.

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[1] Armstrong and Hilditch, Catalytic Processes in Applied Chemistry, p. 33, London.

[2] Russell and Taylor, J. Phys. Chem., *29*, 1325 (1925).

Assuming uniform distribution of the promoter (one molecule of cerium oxide for every 1130 atoms of nickel) upon the surface of a catalyst, such a small change in the surface concentration leads to an approximate ten-fold increase in catalytic activity. Thus it follows that in a nickel catalyst not activated by a promoter, one active nickel atom is accompanied by 11,300 inactive nickel atoms. Thorium and cerium oxide act not only as promoters, but they also serve to increase the surface.

If it is assumed that the function of promoters is chiefly to increase the surface of a catalyst, it is proper to mention here the work of Baxter who showed that small admixtures may increase the surface considerably. Also, he considers that certain oxides prevent the "baking" together of the metal as it is formed from its oxide, the presence of these oxides leading to the formation of a less compact metal and an increase in the surface of the metal in such a way as to cause an increase in its adsorptive ability. From this, it may be concluded that, concomitant with increase in the adsorptive capacity of a metal, there must also be an increase in catalytic activity.

Also, according to my observation, a thin oxide film on the surface of a catalyst has a promoting effect, increasing the active catalytic surface.

As evidence that promoters are instrumental in increasing the surface of a catalyst, mention may be made of the work of Wyckoff and Crittenden[1] who submitted to X-ray examination several ammonia catalysts which had been prepared by reduction with pure hydrogen of magnetic oxide alone and of mixtures of the latter with aluminum oxide and potassium aluminate. The presence of 2–3% of promoter increased the activity of the iron, and also prolonged the life of the catalyst at high temperatures and pressures. These iron catalysts (pure and mixed) were found to possess the same crystal lattice, but the reduced iron mixed with promoter consisted of much smaller crystals than iron without a promoter and the small crystals of iron (in the promoted catalysts) were able to retain their minute structure for a long time. The size of the iron crystals (with promoter) varied from 1×10^{-6} to 1×10^{-3} cm. Evidently, the promoter inhibits the growth of iron crystals.

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[1] Wyckoff and Crittenden, J. Am. Chem. Soc., *47*, 2866 (1925).

Investigations carried out by Bredig and Allolio [1] also furnish information on the rôle of promoters in catalytic reactions. By means of X-rays, these investigators studied metals such as platinum, palladium, and nickel in thin layers, obtained by cathodic dispersion upon glass in an atmosphere of hydrogen and oxygen. The homogeneous layers of these metals obtained in an atmosphere of hydrogen were inactive with respect to a mixture of ethylene and hydrogen and also of oxygen and hydrogen. It was found that hydrogen was present in the crystal lattice of the platinum and palladium, but the nickel obtained under these conditions was different than that obtained in the usual way. The result was different when the dispersion was made in an atmosphere of oxygen. The homogeneous layers of metal oxides were reduced by the subsequent reaction mixture, giving a net-like metal structure which had catalytic activity. No difference between the crystal lattice of active metals obtained in this way and the lattices of inactive compact metals was revealed by the X-ray investigation; the only difference was the size of the crystals. Thus, both investigations substantiate the conclusion that the degree of catalytic activity of a metal has no connection with the structure of the metallic crystal lattice.

It has been pointed out that many investigators assume that promoters, besides increasing the surface of a catalyst, also assist in the formation of active centers upon a catalyst, i.e., of more or less unsaturated atoms on the surface of the metallic crystalline lattice. In the present case, we may assume that a qualitative improvement of the catalyst has occurred. In this regard, it is pertinent to mention the experiments of H. Taylor and Beebel regarding the heat of adsorption upon promoted catalysts. They found that heating nickel at 450° for 21 hours lowered the adsorptive capacity with respect to hydrogen from 17 to 8 cc., and that the total heat of adsorption increased from 14.2 kg. cal. to 20.7 kg. cal. per gram molecule of gas adsorbed. It would appear probable that heating the catalyst up to such a high temperature should make it less active, decreasing the number of active centers and diminishing the heat of adsorption.

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[1] Bredig and Allolio, Z. physik. Chem., *126*, 41 (1927).

Fryling[1] endeavored to explain why one type of adsorption exists for catalysts with promoters and a second type of adsorption for catalysts without promoters. For pure nickel, the heat of adsorption per gram molecule of hydrogen adsorbed is about 30 kg. cal. for the first cc. of gas adsorbed and it decreases with each successive increment until saturation has been reached. The overall heat of adsorption for 20 cc. is about 14 kg. cal. per mol. of hydrogen. On the other hand, with nickel promoted with 13.5% of thorium oxide, the heat of adsorption which is small at first increases with continued adsorption until a maximum is reached and then decreases in a similar manner to that observed for an unpromoted catalyst.

Fryling, in his explanation of the smaller heat of adsorption on a catalyst with a promoter assumes that a dissociation of molecular hydrogen into atomic hydrogen takes place on the active centers of the catalyst which, of course, is accompanied by the absorption of heat. The first portions of adsorbed hydrogen were dissociated into atoms, the process proceeding in the same way as for pure nickel.

From all these data, it may be concluded that promoters not only change the number of active centers, but also influence these centers to produce a special effect.

The deeper we penetrate into the mysteries of catalytic reactions, particularly in the presence of promoters, or in the presence of carriers, the greater the complexity encountered. To solve this mystery, it is necessary to formulate new hypotheses based principally on recent theories concerning atomic structure and on physical phenomena occurring on the surface of a catalyst. Thus, for an explanation of certain catalytic phenomena, especially of auto-catalysis, one is referred to the so-called "interface phenomena," that is, the phenomena occurring between surfaces. As an example of such a phenomenon, there may be cited the observation of Faraday that the crystal hydrates of soda and Glauber's salt are not altered by exposure to air until their surface is damaged. The example given by H. Taylor and Hulett[2] is typical of interface phenomena. At a temperature at which the dissociation of mercuric oxide takes place with evaporation of mercury, the process proceeds very slowly and the dissociation pressure is very small, but in order to accelerate this process so as to be able to measure the dissociation pressure, it is necessary only to create a divided surface by introducing pieces of iron oxide or manganese peroxide. Similar phenomena may also occur in various catalytic processes in which the introduction of a solid catalyst causes an adsorption of two reacting gases coming in contact with one another due to a diffusion on the surface of the catalyst, as well as to an increased concentration of both gases.

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[1] Fryling, J. Phys. Chem., *30*, 818 (1926).

[2] Taylor and Hulett, Proceed. Roy. Soc., *113*, A 81 (1926).

Carriers (kieselguhr, floridin, *et al.*) may play a like rôle; here, also, interface phenomena may occur. These carriers may increase the surface of a catalyst, inhibit its usual crystallization so that it is dispersed in minute crystals, and promote the formation of a greater number of active centers. It is known that a catalyst will lose its active properties when heated to a high temperature but according to the experiments of Pease [1] nickel on a carrier of diatomaceous brick withstood a temperature of 500° without losing its adsorptive ability.

In addition to the foregoing interpretations, recognition should be given to the plausible explanation and to the facts obtained through the experiments of Frumkin [2] with activated carbon. It is known that activated ash-free carbon readily adsorbs acids, but not alkalies. The characteristic adsorptive property of carbon enables this material to combine with the oxygen present on its surface in such a way that it is positively charged. If such a carbon is placed in an atmosphere of hydrogen, its surface is not recharged but, if it is activated by platinum (after activation, the carbon is moistened by a solution of platinum chloride and heated in an atmosphere of hydrogen at 1000°), the carbon acquires the ability to recharge in an atmosphere of hydrogen. When carbon is placed in an atmosphere of hydrogen, it becomes negatively charged, and cations from the solution adhere to the negatively charged surface, e.g., adsorption of alkali replaces adsorption of acid. In an atmosphere of air, such platinized carbon adsorbs acids, but not alkalies. Calculation shows that platinum covers only a few hundredths per cent of the carbon surface, yet its presence markedly changes the adsorptive property of the carbon which is dependent upon the state of the entire carbon surface. Contrary to the theory developed by a number of investigators, particularly Warburg and Rideal, in which it is assumed that the surface of complex heterogeneous catalysts have points exhibiting different catalytic abilities, this investigation shows that surface impregnation of a solid body with small amounts of a substance may influence the properties of the entire surface. Therefore, in the event that carbon acts in the rôle of a catalyst, the state of the entire carbon surface not activated by platinum differs from the state of the entire carbon surface activated by platinum, other conditions being equal.

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[1] Pease, J. Am. Chem. Soc., *45*, 1196, 2235 (1923).

[2] Frumkin and Donde, Sbornik Rabot po chimii, *2*, 1 (1928), Moscow.

After a brief survey of the more important recent investigations concerning the mechanism of catalytic reactions in the presence of promoters, it is desirable to draw a general conclusion in order to see, first, how closely we have approached a true interpretation of these phenomena and, second, to map a future course in this more interesting field of contemporary chemistry.

Of course, it is easier to criticize than to create, and if criticism is justified, it should be presented in such a way as not to devaluate the significance of any scientific work in progress, but rather as a means by which truth may be sought, and as a stepping stone to further investigation.

The investigations conducted since 1920 have rendered, without doubt, valuable service in solving a series of questions in connection with the course of catalytic reactions and have provided much useful information on the application of catalysis in industry. But, as so often repeated, very little consideration has been given the "chemism" of catalytic reactions.

In 1910, when I discovered the joint action of catalysts, the first working hypothesis was proposed for the explanation of the action of promoters in catalytic reactions with reference to the chemical processes taking place. As an explanation of the hydrogenation of camphor by the joint action of nickel oxide and alumina, two assumptions were made, (1) that the saturated hydrocarbon isocamphane is obtained directly from the ketone:

$$C_{10}H_{16}O + 2H_2 \rightarrow C_{10}H_{18} + H_2O$$

(2) that camphor, in the presence of alumina, gives camphene, and camphene, in the presence of nickel oxide, is hydrogenated to isocamphane.

$$C_{10}H_{16}O + H_2 \rightarrow C_{10}H_{18}O$$
$$C_{10}H_{18}O \rightarrow C_{10}H_{16} + H_2O$$
$$C_{10}H_{16} + H_2 \rightarrow C_{10}H_{18}$$

Alumina is a very active substance as evidenced by the fact that in its presence, the temperature for the conversion of camphor to isocamphane is decreased to 190–200°, whereas with nickel oxide alone, no isocamphane is obtained even at 400°.

According to the experimental material at my disposal at that time, catalytic hydrogenation was explained by the participation of active hydrogen liberated *in statu nascendi* by the decomposition of water in the presence of a catalyst. By the participation of a second catalyst, i.e., the joint action of two catalysts, the process may proceed more intensively as the result of an additional amount of energy developed by the reactions caused by the introduction of the second catalyst. The introduction of alumina into a hydrogenation process may be of some assistance because alumina has an affinity for water and may form a series of hydrates, during the formation of which 70,000 cal. of heat are developed. These hydrates dissociate readily and give up water *in statu nascendi* which reacts easily with the hydrogenating catalyst.

Sabatier and Senderens in their endeavor to explain the dehydrating action of aluminum and thorium oxides assumed that these oxides react with alcohols forming complex compounds:

$$Al_2O_3 + 2C_nH_{2n+1}OH \rightarrow Al_2O_2(OC_nH_{2n+1})_2 + H_2O$$

which decomposes, giving either olefins or ethers. Such an assumption should be regarded with suspicion, for it is very doubtful whether alumina can combine with organic compounds.

The fundamental principles of my explanation regarding dehydration catalysis has always been based on the ability of alumina to form hydrates of varying composition, depending upon the temperature, which will actually react with organic substances. But, having no experimental evidence with which to determine the character of the intermediate compounds, I have not proposed a new hypothesis. At present, as will be seen in the following chapter, there is sufficient data on hand to justify the proposal of a new hypothesis concerning the rôle of alumina in dehydration catalysis.

It is assumed that one of the active hydrates of alumina corresponds to an aluminate salt, having the formula $AlO(OH)$. This hydrate may react with alcohol at a high temperature to give a complex ester:

$$AlO(OH) + C_nH_{2n+1}OH \rightarrow H_2O + AlO(O{-}C_nH_{2n+1})$$

which, by decomposition, may give an olefin, regenerating the hydrate of alumina:

$$AlO(O\text{—}C_nH_{2n+1}) \rightarrow C_nH_{2n} + AlO(OH)$$

If the temperature is low, the complex alumina hydrate ester will decompose with separation of a simple ether:

$$2AlO(OC_nH_{2n+1}) \rightarrow C_nH_{2n+1}\text{—}O\text{—}C_nH_{2n+1} + H_2O$$

If we adopt this hypothesis, and its proof is substantiated by a series of experiments (cf. "On the Theory of Dehydration and Polymerization Catalysis"), the rôle of alumina in the hydrogenation of camphor by nickel oxide will be clarified.

The first phase of the reaction is the hydrogenation of camphor to borneol:

$$C_{10}H_{16}O + H_2 \rightarrow C_{10}H_{18}O$$

The second phase is the formation of the alumina hydrate ester.

$$AlO(OH) + C_{10}H_{18}O \rightarrow AlO(OC_{10}H_{17}) + H_2O$$

By dissociation of the ester, the hydrogenation of the radical $C_{10}H_{17}$ to isocamphane proceeds with great ease under the influence of nickel oxide:

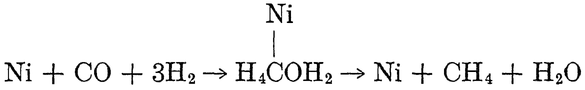
$$AlO(OC_{10}H_{17}) + H_2 \rightarrow AlO(OH) + C_{10}H_{18}$$

If a weak catalyst, such as copper oxide, is substituted for the very active catalyst, nickel oxide, the results obtained with the $CuO\text{—}Al_2O_3$ will be found to differ from those obtained with $NiO\text{—}Al_2O_3$. As shown experimentally, the conversion of the ketonic group into the alcoholic group proceeds easily under the influence of copper oxide. Therefore, the first phase of the reaction will be the conversion of camphor to borneol. Similarly, the hydrate of aluminum forms a complex ester with borneol but because of the absence of a strong hydrogenating catalyst, the complex ester is unable to undergo hydrogenation; however, under the influence of alumina, this complex ester undergoes dehydration with separation of an unsaturated hydrocarbon, camphene.

$$AlO(OC_{10}H_{17}) \rightarrow AlO(OH) + C_{10}H_{16}$$

Evidence for this mechanism will be presented later. A study of catalytic processes in general, and of catalytic reactions in the presence of promoters particularly, is of the utmost importance in determining the course of a catalytic reaction. Besides the influence of its chemical properties, the rôle of a promoter consists in increasing the surface of a catalyst (thereby facilitating adsorption), preventing the formation of large crystals and of "baking together," and prolonging the life of the catalyst. Catalytic reactions, proceeding at enormous speeds, are "capricious" processes which may be stopped abruptly by very small changes in the conditions, or changed completely in direction, as shown by Langmuir's experiments.

Of course, it is possible to give a chemical explanation for catalytic reactions occurring in the presence of a single catalyst, or in the presence of two catalysts, only after experimental data have conclusively confirmed the suppositions concerning the course of the reaction. For example, Medforth's [1] explanation of the hydrogenation of carbon monoxide under the influence of metallic nickel and promoters is based upon insufficient experimental evidence. Medforth assumes that the hydrogenation of carbon monoxide in the presence of a nickel catalyst promoted with thorium oxide occurs with the formation of the following intermediate complex whose formation has not been proven experimentally; therefore, the explanation is doubtful.



$$Ni + CO + 3H_2 \rightarrow H_4\overset{\overset{\displaystyle Ni}{|}}{C}OH_2 \rightarrow Ni + CH_4 + H_2O$$

If we agree with Medforth that the first phase consists in the reaction of carbon monoxide with hydrogen to give formaldehyde and then methyl alcohol, the latter phase of the reaction, under the influence of the dehydration catalyst, should lead to the formation of methyl ether as shown experimentally by Ipatieff.

$$2CH_3OH \rightarrow H_2O + CH_3{-}O{-}CH_3$$

This ether is quite stable, very little decomposition taking place at 520°, carbon monoxide and hydrogen being present in the gas from the decomposition.

If it is assumed that methyl alcohol decomposes under the influence of alumina to form the methylene radical, CH_2, we should expect at least small amounts of ethylene and ethane. Actually, according to experimental evidence, such an assumption is unjustified.

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[1] Medforth, J. Chem. Soc., *123*, 1452 (1923).

I propose that methyl alcohol is first formed from carbon monoxide and hydrogen (proved experimentally). Then an ester is formed between alumina hydrate and methanol, which under the influence of the strong hydrogenation catalyst, gives methane and regenerates the hydrate of alumina. The entire reaction is analogous to the hydrogenation of camphor.

$$\mathrm{AlO(OH)} + \mathrm{CH_3OH} \rightarrow \mathrm{AlO(OCH_3)} + \mathrm{H_2O}$$

$$\mathrm{AlO(OCH_3)} + \mathrm{H_2} \rightarrow \mathrm{AlO(OH)} + \mathrm{CH_4}$$

In Medforth's investigation, the composition of the gas and the products formed in the reactions under varying conditions were incompletely studied, whereas I have based my explanation of the action of promoters in the reduction of carbon monoxide to methane upon experimental evidence. The explanation offered for the joint action of metallic catalysts upon organic compounds is not unlike the proposals given at the present time as an interpretation of the acceleration of the oxidizing action of hydrogen peroxide on the salts of iron sub-oxide and the freeing of active oxygen from peroxides under the influence of certain salts ($FeSO_4$). As shown by the experiments of Melikov and Pissarchevsky, the acceleration produced in the oxidation of salts is not due to their absorption of oxygen from the atmosphere but rather to the formation of unstable peroxidic compounds which give up the active oxygen.

A similar hypothesis was also developed by Bach as an explanation of the hydrolytic reduction and oxidation processes of metabolism occurring in living organisms. The theory of the action of oxidases developed principally by Bach and Schaadi assumes the existence of two organic catalysts or ferments in phenolase which produce the oxidation processes. The first, oxygenase, oxidizes readily, forms peroxides, and may transfer the active oxygen to the substrate, and the other, peroxidase, similar to metallic salts, accelerates the passage of oxygen from the oxygenase to the substrate. Inasmuch as the theoretical action of these two ferments correspond to the actual action, it follows that by substituting certain salts, particularly those of aluminum, for the peroxidase, an acceleration of the oxidation process is obtained which is identical with that obtained by the addition of peroxidase.

The *perhydrases* (reduction ferments) of Bach produce a similar joint action; the *chromogens* of Palladin, as well as other ferments, accelerate the oxidation and reduction processes based on the decomposition of water. These processes are analogous to the reactions previously indicated for the simultaneous oxidation of aldehydes and the reduction of methylene blue under the influence of palladium or organic ferments in the presence of water.

In addition to these hydrolytic reduction and oxidation processes in which the function of an oxide is fulfilled by the oxygen of the water present in plant and animal organisms, there are also hydration, reduction, and oxidation processes to which belong the hydrolysis and oxidation of albumins, *et al.* Such processes may also occur under the influence of the joint action of catalysts: mineral salts, acids, and alkalies, or organic ferments such as pepsin, pancreatin, etc. There is marked similarity between the metabolic processes of catabolism and anabolism and the reduction reactions of ketones, aldehydes, alcohols, and perhaps of other organic compounds which take place under the influence of two catalysts producing hydration-reduction processes.

By introducing reactions influenced by the joint action of two catalysts into the field of catalysis, we have obtained new methods for the formation of organic compounds, the character of which depends upon the type of the catalyst.

DEHYDRATION, POLYMERIZATION, AND ALKYLATION CATALYSIS

Proportionately greater significance is attached to a scientific theory if it concerns itself with plausible, self-explanatory phenomena and if it is able to make predictions confirmable by experiments. A theory or hypothesis loses prestige if it fails to suggest new ideas. In the broad fields of catalytic reactions involving oxidation, reduction, hydration, polymerization, etc., there is no general theory which embodies all the phenomena of catalysis and at the same time unifies all the chemical actions involved. Assuming that all the natural forces operating in catalysis are identical, we must take into consideration the fact that catalytic reactions occurring within molecules have all the characteristics of chemical transformations. Now the question is, how do these processes proceed, and what rôle is played by the catalyst, which at the termination of the process remains unchanged although, of course, it is sometimes altered by side reactions. After consideration of all known catalytic reactions, it is seen that they may be grouped into three classes.

In the *First Group* may be included those catalytic reactions which are explainable (in some instances conclusively) by the formation of intermediate compounds between the catalyst and the acting substances, the catalyst functioning as a chemical reactant. But, since the intermediate compound is unstable under the given conditions, the catalyst is regenerated. Thus, it repeats the reaction many times; in other words, a catalyst is a reaction multiplier.[1]

In the *Second Group* may be included those catalytic reactions in which the formation of intermediate compounds is doubtful and the rôle of the catalyst, from the viewpoint of "chemism," is not understood. Such reactions should be termed "*Eka*"-[2] *catalytic* until such time when their chemical mechanism is known. As an example of such catalysis may be cited the separation of lead hydrate from lead nitrate solution contained in a gold or quartz tube under hydrogen pressure.[3] Three allotropic crystalline modifications of lead hydrate were obtained and we were unable to determine the effect of the walls of the tube upon the chemical reaction. This action may rightly be called an eka-catalytic reaction. Countless other examples can be enumerated.

In the *Third Group* may be included those catalytic reactions involving photo-catalysis and other reactions occurring in the presence of light energy or of any other energy. This type of catalysis may be called "physical" catalysis.

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[1] The term "catalysis," introduced by Berzelius is, according to my opinion, a misnomer; it does not portray the fundamental idea of catalytic reactions.

There is a similarity between the Greek words catalysis and analysis, but the prefix "cata" is interpreted "down." Catalysis, as defined in a very restricted sense, implies a decomposition process, a process involving a type of reaction from the complex to the simple. As is known today, catalytic reactions not only catalyze, but also synthesize; therefore, the term "catalysis" is not suitable as a designation for the latter phenomenon.

Mitcherlich applied the term "contact" phenomena. This definition was used in Russia for a long time, practically up to the beginning of the twentieth century. "Contact" phenomena is also inadequate for, in general, all chemical reactions are contact reactions.

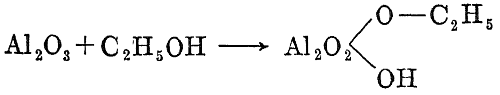
If we accept the viewpoint of the theory of intermediate reactions between catalyst and the reacting substance, then it would be logical to designate these reactions as "multiplication reactions" and catalysts as "multipliers" or multi-actors. And if we cannot concur in this nomenclature we must seek one that is more fitting. At present, it appears very difficult to find a more appropriate term for catalytic reactions.

[2] Eka-catalytic is unknown-catalytic.

[3] Ipatieff and Ipatieff, Jr., Ber., *61*, 624 (1928).

Referring again to a discussion of the theoretical principles of catalytic reactions: dehydration, polymerization, and alkylation are to be classified (according to experimental material at our disposal) in the First Group because the formation of intermediate compounds has been definitely proven in certain cases.

When a supposition concerning the formation of intermediate compounds is expressed, it is well to illustrate it by equations which, of course, must be confirmed, either by experimental data, or by the chemical properties of the catalyst and its probable action upon the substance participating in the reaction. It is to be regretted that many investigators explain catalytic reactions by means of intermediate products, whose formation is not substantiated by any of the methods indicated. For example, as an explanation of the catalytic dehydration of alcohols by means of alumina, Senderens[1] proposes the following equation:



$$Al_2O_3 + C_2H_5OH \longrightarrow Al_2O_2\begin{cases} O-C_2H_5 \\ OH \end{cases}$$

There is no evidence for the formation of such a complex. The reaction itself is little understood and it is doubtful if the assumption of such a complex would assist in predicting new catalysts for catalytic dehydration. Perhaps it would be easier to explain this dehydration reaction by means of the alcohol aluminates, but even then it would necessitate proving that the aluminates decompose into olefins and alumina, for which at present there is no evidence.

Alumina prepared in a definite way has an affinity for water and removes it from organic compounds containing the hydroxyl group. In 1903, attention was drawn to the fact that alumina must contain a certain amount of combined water in order that the dehydration of alcohols should take place at comparatively low temperature. According to my experiments, a parallel exists between the action of sulphuric acid and alumina in removing water from organic compounds containing the hydroxyl group. As the experimental data were insufficient to establish a hypothesis regarding the formation of intermediate products, I restricted myself to the above-mentioned explanation of this catalytic reaction.

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[1] Senderens, Bull. soc. chim., (4), *1*, 692 (1907).

Investigations conducted in recent years on the polymerization of olefins and the alkylation of organic compounds in the presence of various catalysts, as well as the addition of olefins to acids yielded a wealth of experimental material which permitted generalization on all the reactions indicated and led to the proposal of a hypothesis explaining and summarizing catalytic dehydration and polymerization.

At the beginning of these investigations the action of sulphuric acid upon olefins served as a means of analyzing hydrocarbon mixtures. Although a number of investigators claimed sulphuric acid could not be used for this purpose, the literature indicates that it is still used for this purpose, principally because other methods of determining olefins are still more unreliable.

Experiments by Ipatieff and Pines [1] showed that sulphuric acid (92–96%) not only dissolves olefins to form esters, but that sulphuric acid decomposes esters, forming polymers and saturated hydrocarbons. If both an olefin and a benzene hydrocarbon are present, the benzene hydrocarbon is alkylated in the presence of the sulphuric acid which serves as the catalyst.

Previous to our investigations, findings had been published by Brooks and Humphrey,[2] Norris and Joubert,[3] and Ormandy and Craven,[4] but only Ormandy and Craven studied the polymerization products formed by treatment of olefins with sulphuric acid. Their assertions were based on the indices of refraction which gave the indication that chiefly saturated hydrocarbons were formed by the polymerization of olefins. Their one analysis of the hydrocarbons corresponded to the formula C_9H_{20}, but no explanation was given as to the origin of these saturated hydrocarbons.

In studying the action of sulphuric acid upon amylene in the presence of benzene, they observed a condensation reaction but they did not investigate the reaction products. They concluded inaccurately that: "In the presence of olefins, aromatics are not entirely removed by sulphuric acid but partly condensed with the hydrocarbons from the olefins." It is clear that they supposed certain hydrocarbons were formed by the condensation of olefin polymers with benzene.

In our investigations, the action of sulphuric acid upon olefins in the presence of various hydrocarbons was confirmed by reactions and analyses which showed that in the majority of cases sulphuric acid cannot be used for the quantitative determination of olefins and that the velocity of alkylation of aromatics by olefins is greater than the velocity of olefin polymerization. Thus, in the presence of benzene, olefins undergo no polymerization under the influence of sulphuric acid (concentration not below 90%) at 0°, but are completely consumed in alkylating the benzene. This information was our incentive for studying the mechanism of the polymerization reaction so as to discover the reason for the formation of saturated hydrocarbons and also for investigating the alkylation of benzene hydrocarbons by olefins more thoroughly.

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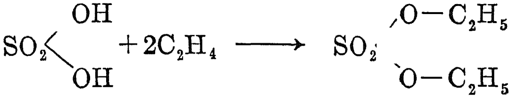
[1] Refer to chapter on polymerization and alkylation.

[2] Brooks and Humphrey, J. Am. Chem. Soc., *40*, 482 (1928).

[3] Norris and Joubert, J. Am. Chem. Soc., *39*, 873 (1927).

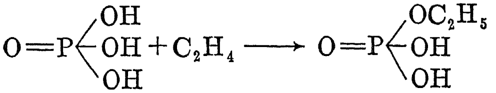
[4] Ormandy and Craven, J. Inst. Petroleum. Tech., *13*, 311 (1927).

Accordingly, the addition of olefins to sulphuric and phosphoric acids was studied under various conditions both at atmospheric and superatmospheric pressure. Olefins combined with the acids to form complex esters under all the experimental conditions employed, but the yield of ester was greater under superatmospheric pressure than under atmospheric pressure. Under pressure at 30–70° ethylene gives diethyl sulphate almost quantitatively.



$$SO_2\left<\begin{matrix}OH\\OH\end{matrix}\right. + 2C_2H_4 \longrightarrow SO_2\left<\begin{matrix}O-C_2H_5\\O-C_2H_5\end{matrix}\right.$$

Phosphoric acid under pressure at 200° gives a large yield of the mono-ethyl ester of phosphoric acid:

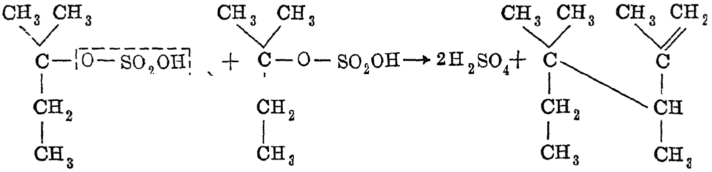


$$O{=}P\left<\begin{matrix}OH\\OH\\OH\end{matrix}\right. + C_2H_4 \longrightarrow O{=}P\left<\begin{matrix}OC_2H_5\\OH\\OH\end{matrix}\right.$$

Polymerization

From the experimental data obtained, as well as with reference to the literature as a whole, it was concluded that the most plausible explanation for the polymerization of olefins under the influence of acids is the formation of various acid esters followed by their decomposition chiefly into unsaturated hydrocarbons but also into saturated hydrocarbons.

Previously, it had been assumed that only mono-esters were formed by the reaction of an olefin with sulphuric acid. Two molecules of mono-esters reacting with one another are able to regenerate sulphuric acid and form a polymer:



Because of the ability of the sulphuric acid radical to take away an atom of hydrogen from different atoms of carbon of another molecule of mono-ester, various isomeric hydrocarbons are formed. It is difficult to explain the formation of a paraffinic hydrocarbon by means of mono-esters. It would be necessary to assume the elimination of sulphuric acid between two molecules of mono-ester to form two alkyl radicals and oxygen, the radicals subsequently combining to form a saturated hydrocarbon.

Perhaps the formation of the saturated hydrocarbons would be better understood if it is assumed that a di-ester of sulphuric acid is formed which (being an unstable ester with a tertiary carbon atom) decomposes easily with the separation of a saturated hydrocarbon and an atom of oxygen *in statu nascendi:*

$$C_5H_{11}—O—SO_2—O—C_5H_{11} \rightarrow SO_3 + O + (C_5H_{11})_2$$

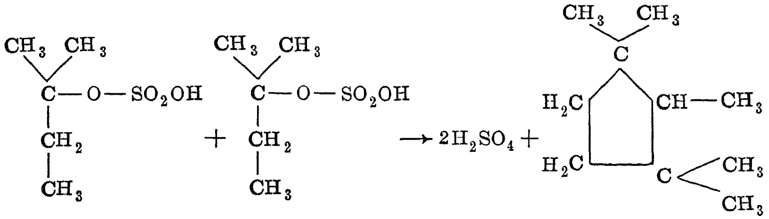
Such a decomposition resulting in the formation of saturated hydrocarbons also occurs to a very limited extent with esters containing the lower molecular weight radicals. The liberated oxygen may oxidize the hydrocarbons forming oxygenated organic compounds such as alcohols. The separation of sulphur dioxide and the liberation of oxygen during the polymerization of olefins may serve as indication of the decomposition of esters of sulphuric acid.

Our latest investigations on the action of catalysts (phosphoric acid, aluminum chloride, etc.) have shown that olefins can be isomerized into naphthenes and the latter may lose hydrogen to form unsaturated mono- or dicyclic hydrocarbons. The liberated hydrogen, *in statu nascendi,* hydrogenates olefins to paraffins. This reaction takes place in the presence of phosphoric acid and it is logical to assume that it also takes place in the presence of sulphuric acid.

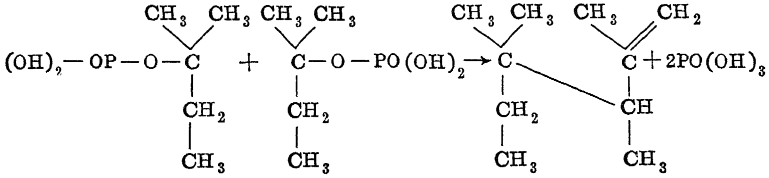
If this hypothesis be accepted it is easy to explain the fate of the oxygen liberated during the decomposition of the dialkyl esters of sulphuric acid, namely, the oxygen and hydrogen unite to form water which reacts with the sulphur trioxide to regenerate the sulphuric acid catalyst.

It is inferred that an equilibrium exists between sulphuric acid and the mono- and di-esters, which depends chiefly upon the structure of the olefin and upon the strength of the acid.

Analysis of the hydrocarbons obtained by polymerization, e.g., polymers formed from amylene in the presence of sulphuric acid, shows that saturated hydrocarbons are present only in the first fractions, the higher fractions being made up of hydrocarbons of the formula C_nH_{2n}, and consisting principally of olefins as indicated by their reactions. It is a debated question whether naphthenes are present in these hydrocarbons. In the absence of contradicting evidence it may be assumed that during decomposition of the heavier molecules of sulphuric acid esters a closing of the ring may occur according to the following scheme:



Application of this hypothesis to the polymerization reactions of olefins under the influence of phosphoric acid gives the following scheme:



It is assumed that the reaction proceeds in such a way that two molecules of mono-amyl ester react to produce a molecule of olefin and phosphoric acid. The resulting polymer may consist of various isomers since the hydrogen split out by the phosphoric acid radical may be taken from different carbons.

A detailed account will appear in the chapter on polymerization, but here it is to be noted that phosphoric acid is a true catalyst for the polymerization of olefins. When the reaction is run at low temperatures, only olefins are produced:

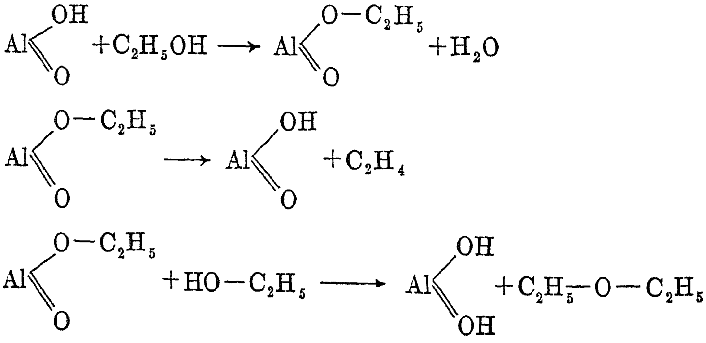
$$C_3H_6 \rightarrow C_6H_{12} \rightarrow C_9H_{18} \rightarrow C_{12}H_{24}, \text{ etc.}$$

If the temperature of the reaction is increased, paraffinic hydrocarbons will be found in the lower fractions of the polymerization products and hydrocarbons poorer in hydrogen than olefins will be present in the higher fractions, i.e., monocyclic or polycyclic hydrocarbons containing an unsaturated side chain or a ring of terpenic character.

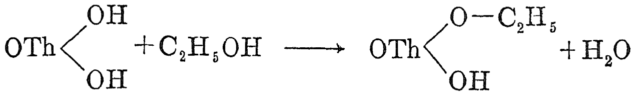
Dehydration

In view of the results obtained in the polymerization of olefins, it is evident that catalysts which bring about polymerization are also dehydration catalysts. The dehydration of alcohols by sulphuric acid is attributed to the formation of unstable esters which decompose to give the corresponding olefins.

In the case of alumina, thoria and other catalysts, it is assumed that hydrates are active factors, leading to the formation of unstable esters. If it be assumed that alumina forms a hydrate corresponding to sodium aluminate ($NaAlO_2$), dehydration may by represented by the following equations, and it will depend upon the temperature whether the final product is olefin or ether. One cannot fail to see a complete analogy between this reaction and the action of sulphuric acid upon an alcohol.

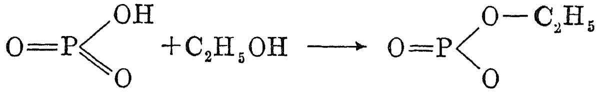


At a higher temperature, polymerization also takes place with the same catalyst. Likewise, by assuming that thorium oxide exists as the hydrate, $ThO(OH)_2$, mono-esters and perhaps di-esters are possible intermediate products which would decompose to give either ethylene or ethyl ether:



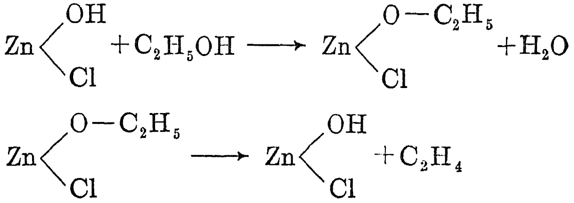
$$OTh\begin{cases}OH\\OH\end{cases} + C_2H_5OH \longrightarrow OTh\begin{cases}O-C_2H_5\\OH\end{cases} + H_2O$$

Orthophosphoric acid may be converted into metaphosphoric acid which gives mono-esters:



$$O=P\begin{cases}OH\\O\end{cases} + C_2H_5OH \longrightarrow O=P\begin{cases}O-C_2H_5\\O\end{cases}$$

Zinc chloride plays a dual rôle as catalyst. In the presence of water it forms zinc oxychloride which acts as a dehydration catalyst:



$$Zn\begin{cases}OH\\Cl\end{cases} + C_2H_5OH \longrightarrow Zn\begin{cases}O-C_2H_5\\Cl\end{cases} + H_2O$$

$$Zn\begin{cases}O-C_2H_5\\Cl\end{cases} \longrightarrow Zn\begin{cases}OH\\Cl\end{cases} + C_2H_4$$

At a higher temperature (about 240°) zinc chloride, as shown by my experiments,[1] gives polymerization products under superatmospheric pressure. The experiments made by Kondakov [2] with zinc chloride and olefins furnish excellent evidence for our hypothesis. Kondakov succeeded in showing that (1) zinc chloride forms crystalline compounds with olefins having a tertiary carbon atom; (2) this reaction may occur only in the presence of water and at a very low temperature; (3) that the decomposition of these compounds (esters) produces polymers (in case of amylene, diamylene) as well as alcohol.

Experiments were carried out with phosphoric acid to test the correctness of our hypothesis which explains dehydration and polymerization as depending on the formation of complex esters by reaction of the olefin with a catalyst containing the hydroxyl group.

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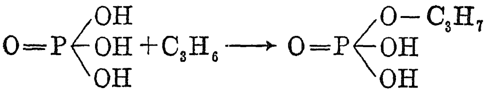
[1] According to the literature good polymerization of olefins in the presence of zinc chloride occurs only when this salt contains a small amount of water. See Ipatieff and Routala, Ber., *46*, 1748 (1913).

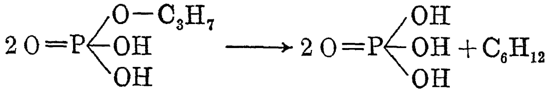
[2] Kondakov, J. Russ. Phys. Chem. Soc., *25*, 442 (1893); J. prakt. Chem., (2), *54*, 466 (1896).

The mono-propyl ester of phosphoric acid was formed when this acid (95–100%) and propylene were heated at 125° in a pyrex liner contained in a rotating autoclave:



$$O{=}P\begin{matrix}\diagup OH\\ -OH\\ \diagdown OH\end{matrix} + C_3H_6 \longrightarrow O{=}P\begin{matrix}\diagup O-C_3H_7\\ -OH\\ \diagdown OH\end{matrix}$$

When the mono-propyl ester was heated to 150°, it decomposed to form a light, transparent layer over the phosphoric acid. This layer consisted entirely of olefins, principally hexylene and nonylene. The same liquid product was obtained in one step by heating propylene and phosphoric acid under pressure at 150°.



$$2\,O{=}P\begin{matrix}\diagup O-C_3H_7\\ -OH\\ \diagdown OH\end{matrix} \longrightarrow 2\,O{=}P\begin{matrix}\diagup OH\\ -OH\\ \diagdown OH\end{matrix} + C_6H_{12}$$

Thus, in this catalytic reaction an intermediate product is formed which decomposes and regenerates the catalyst. The reaction of sulphuric acid upon olefins is analogous. The mono- and disulphates formed decompose to give either alcohols or polymers of olefins, depending upon the structure of the original olefin, the concentration of the acid, temperature, etc. Since sulphuric acid is a strong oxidizing agent and its esters are much more stable than the esters of phosphoric acid, the reaction of sulphuric acid with many olefins does not proceed smoothly. Therefore, polymerization by means of sulphuric acid could be studied only with certain olefins, principally those containing the $—C{=}CH_2$ group (isobutylene, amylene) which had previously been done by Butlerov, Kondakov, and Lebedev.

Phosphoric acid is a much more suitable catalyst because it does not oxidize organic compounds, and its esters are unstable and, therefore, do not complicate the reaction. At low temperatures (below 200°) practically only olefins are obtained in the polymerization of gaseous olefins with phosphoric acid as catalyst;[1]

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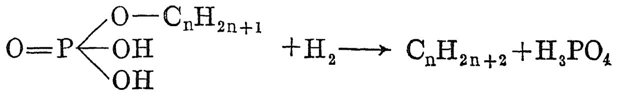
[1] Our recent investigations on the polymerization of ethylene under pressure in the presence of phosphoric acid showed that olefins at the moment of their formation could be isomerized into naphthenes. This reaction takes place only with certain olefins which have a sufficient length of carbon chain and special constitution. The naphthene, dimethylcyclohexane, was found in the 120–130° fraction of the

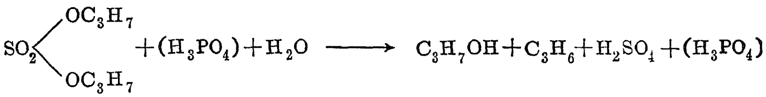
at higher temperature and under pressure, the low boiling fractions contain paraffins and the high boiling fractions contain naphthenes and aromatic hydrocarbons. The hydrogen necessary for the formation of the paraffins comes from the formation of unsaturated cyclic hydrocarbons, probably having the formula C_nH_{2n-6} and C_nH_{2n-8}, since the higher fractions contain considerably less hydrogen than required by the formula C_nH_{2n}. The reactions may be illustrated by the following equations:

$$n(H_3PO_4\cdot C_nH_{2n}) \longrightarrow n(C_nH_{2n-2}) + nH_3PO_4 + nH_2$$



$$O{=}P\left\langle\begin{array}{l}O-C_nH_{2n+1}\\OH\\OH\end{array}\right. + H_2 \longrightarrow C_nH_{2n+2} + H_3PO_4$$

It is interesting to note that phosphoric acid is a catalyst for the decomposition of both the mono- and the di-esters of sulphuric acid, the esters decomposing partly into alcohol and partly into polymer.



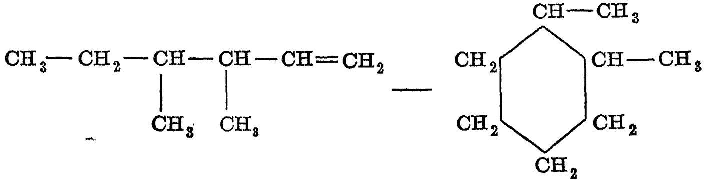
$$SO_2\left\langle\begin{array}{l}OC_3H_7\\OC_3H_7\end{array}\right. + (H_3PO_4) + H_2O \longrightarrow C_3H_7OH + C_3H_6 + H_2SO_4 + (H_3PO_4)$$

$$nC_3H_6 + (H_3PO_4) \longrightarrow (C_3H_6)_n + H_3PO_4$$

This reaction proceeds to completion since the very small amount of phosphoric ester which is formed decomposes at once into olefin which polymerizes under the influence of phosphoric acid. This reaction takes place at 80–90° and a very small amount of phosphoric acid decomposes a large amount of sulphate esters. The sulphate esters present in sulphuric acid treated gasoline may be completely eliminated by this reaction.

Experiments confirmed the correctness of the hypothesis assumed as explanation of the catalytic dehydration and polymerization of olefins. Furthermore, it can be predicted from this hypothesis

ethylene polymer. According to the analytical figures this fraction contained an octene, probably 3, 4-dimethyl hexene-1.



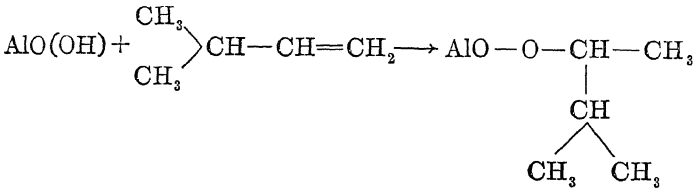
that other acids may also serve as catalysts for the polymerization of olefins. It has been shown experimentally that perchloric acid and trichloracetic acid polymerize olefins. For example, amylene heated at 190° in the presence of trichloracetic acid under 43 atmospheres of nitrogen pressure gave a considerable amount of diamylene.

ISOMERIZATION

This hypothesis is also applicable as an explanation for catalytic isomerization. My experiments established the fact that isopropylethylene isomerizes into trimethylethylene under the influence of alumina. If it is considered that the migration of hydrogen atoms within the hydrocarbon molecule does not sufficiently explain this phenomenon, then the application of the hypothesis involving the formation of intermediate esters of the hydrocarbon with alumina hydrate [AlO(OH)] will make the reaction more readily understandable. *The addition of an olefin to an acid to form an ester proceeds in such a way that an atom of oxygen combines with the carbon atom which is least hydrogenated.*

This rule,[1] as it will be seen further, is confirmed by many examples.

In the present case the equation for the reaction is:



By the decomposition of this ester, alumina and trimethylethylene are obtained.

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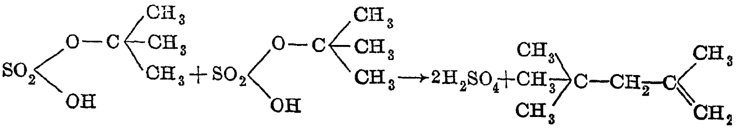
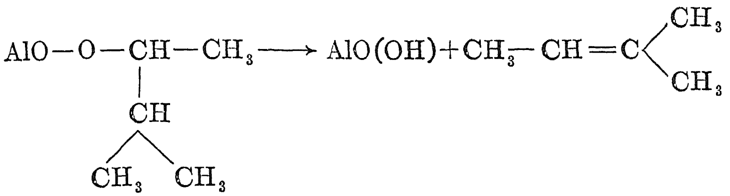
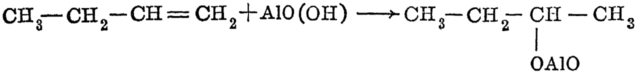
[1] This regularity is also confirmed by the structure of the chief product of the polymerization of isobutylene under the influence of sulphuric acid first observed by Butlerov and repeated here.

According to the rule indicated, the structure of di-isobutylene should be:

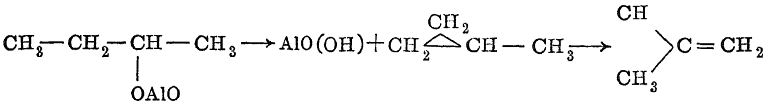




The isomerization of 1-butene to isobutylene may be explained in a similar manner if it is assumed that the hydrogen atom is not removed from the neighboring carbon atom because of the fact that a saturated hydrocarbon is obtained which isomerizes readily into an olefin formed *in statu nascendi:*



$$CH_3-CH_2-CH=CH_2+AlO(OH) \longrightarrow CH_3-CH_2-\underset{OAlO}{\underset{|}{CH}}-CH_3$$



It appears more difficult to explain the isomerization of naphthenes to olefins by means of this hypothesis, and particularly the catalytic conversion of cyclohexane into methyl cyclopentane under the influence of alumina, a change observed in experiments conducted by Ipatieff and Dovgelevitch. Such reactions should be called *eka-catalytic.* An explanation for these reactions can be given only after sufficient experimental data have been accumulated.

ALKYLATION

As previously indicated, the action of sulphuric acid upon olefins in the presence of benzene hydrocarbons causes a condensation reaction between the olefin and the aromatic hydrocarbon. Ormandy assumed that the sulphuric acid caused the condensation of the olefin polymer with benzene. With this brief notice of this interesting reaction, Ormandy neglected to inform himself that the literature already contained reports by Spilker [1] and Brochet [2] who, forty years ago, showed that sulphuric acid caused the condensation of olefins with benzene hydrocarbons to give substituted benzenes. Since this reaction was not considered, the sulphuric acid method of determining olefins gave incorrect results when applied to hydrocarbon mixtures containing both olefins and benzene hydrocarbons. Ipatieff and Pines [1] studied in detail the effect of sulphuric acid upon a mixture of amylene and benzene at 0°, and established the fact that alkylation of benzene took place with the formation of mono-, di-, and tri-amyl benzenes:

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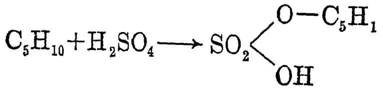
[1] Spilker, Ber., *23*, 3169 (1890).

[2] Brochet, Compt. rend., *117*, 115 (1893).

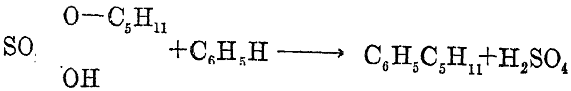
$$C_6H_6 + C_5H_{10} \rightarrow C_6H_5C_5H_{11}$$

It was further ascertained that the velocity of this reaction is greater than that of the polymerization of amylene to diamylene. No olefins are obtained in the alkylation of benzene, as indicated by the non-reactivity of the product with potassium permanganate solution. Brochet (1893), who first investigated the reaction of hexylene with benzene in the presence of sulphuric acid, indicated that the reaction of *amylene* with benzene in the presence of sulphuric acid produced so much tar that the product could not be separated for analysis. Without making further experiments, Brochet considered this reaction a general one for all olefins. However, our experiments showed that the reaction with amylene occurs without any tar formation and that ethylene does not react under these conditions. In the meantime, other gaseous olefins were found to alkylate benzene with enormous velocities, giving substituted benzene. Thus Ipatieff and Corson obtained mono-, di-, and tri-propyl benzenes and various substituted butyl benzenes. (Refer to chapter on alkylation.) The chief product of the reaction, the substituted benzene, was accompanied by sulphuric acid ester and thus it appears logical to apply the hypothesis proposed for polymerization and dehydration also as an explanation of alkylation.

The olefin hydrocarbon forms alkyl sulphate which reacts with the benzene nucleus giving substituted benzene and regenerating sulphuric acid:

(I) 

$$C_5H_{10}+H_2SO_4 \longrightarrow SO_2\begin{cases} O-C_5H_1 \\ OH \end{cases}$$

(II) 

$$SO\begin{cases} O-C_5H_{11} \\ OH \end{cases} + C_6H_5H \longrightarrow C_6H_5C_5H_{11}+H_2SO_4$$

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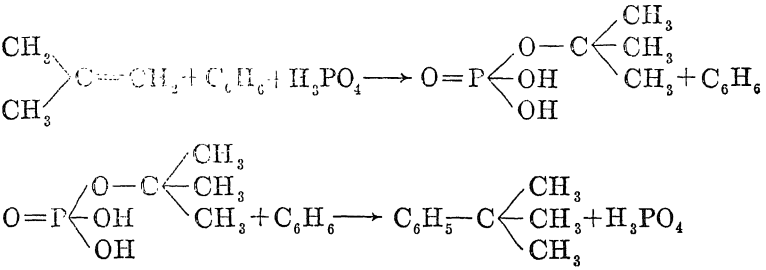
[1] Ipatieff and Pines, Research Laboratories, Universal Oil Products Company.

It is possible that sulphuric acid accelerates the substitution of the hydrogen in the benzene ring. It may be that benzene forms an unstable complex with sulphuric acid which renders the hydrogen atoms of the benzene more mobile.

If the hypothesis of the formation of esters between catalyst and olefin is applicable to alkylation, then polymerization and dehydration catalysts must also be alkylation catalysts. Experiments conducted in the Research Laboratories of the Universal Oil Products Company, Riverside, Illinois, in 1932 and 1933, confirmed this assumption. Ethylene and amylene, under pressure and in the presence of perchloric acid were found to alkylate benzene to form ethyl and amyl benzenes, respectively. In studying the alkylation of benzene by isobutylene at ordinary pressure in the presence of phosphoric acid, Ipatieff and Corson found that there was also polymerization of isobutylene, the reaction product consisting of a mixture of isobutylene polymers and tert-butyl benzene.



$$\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\!>\mathrm{C{=}CH_2} + \mathrm{C_6H_6} + \mathrm{H_3PO_4} \longrightarrow \mathrm{O{=}P}\begin{cases}\mathrm{O-C}\begin{cases}\mathrm{CH_3}\\ \mathrm{CH_3}\\ \mathrm{CH_3}\end{cases}\\ \mathrm{OH}\\ \mathrm{OH}\end{cases} + \mathrm{C_6H_6}$$

$$\mathrm{O{=}P}\begin{cases}\mathrm{O-C}\begin{cases}\mathrm{CH_3}\\ \mathrm{CH_3}\\ \mathrm{CH_3}\end{cases}\\ \mathrm{OH}\\ \mathrm{OH}\end{cases} + \mathrm{C_6H_6} \longrightarrow \mathrm{C_6H_5-C}\begin{cases}\mathrm{CH_3}\\ \mathrm{CH_3}\\ \mathrm{CH_3}\end{cases} + \mathrm{H_3PO_4}$$

The addition of isobutylene to phosphoric acid proceeds according to the rule previously indicated, namely, *oxygen combines with the least hydrogenated carbon atom.*

Using phosphoric acid as catalyst, Ipatieff and Komarewsky[1] obtained alkyl-substituted naphthalenes and fluorenes, the reaction being made under pressure. The advantage of phosphoric over sulphuric acid was marked since sulpho acids were not formed and there was much less tarry material obtained.

After establishing the possibility of alkylating the aromatic nucleus by means of various catalysts, attention was centered on the alkylation of other aromatic compounds, first of all phenols.

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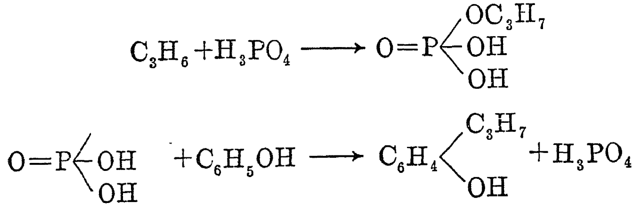
[1] In order to avoid the presence of alkyl sulphates in the alkylated product, the influence of the addition of phosphoric acid to sulphuric acid was studied. Experiments showed that a destruction of esters took place under these conditions and that an excellent yield of pure substituted benzene hydrocarbon was obtained.

Koenigs [1] was the first to alkylate phenols with olefins in the presence of sulphuric acid. Using a mixture of amylene and phenol, he obtained substituted phenols. Corson undertook the alkylation of phenol by means of amylene in the presence of sulphuric acid and obtained amyl phenol. But the yield of substituted phenol was small since this reaction was accompanied by sulphurization and the formation of tarry products. Therefore, further alkylation of phenols was carried out with phosphoric acid as the catalyst. Experiments by Pines on the alkylation of mono-, di-, and tri-hydric phenols in the presence of phosphoric acid showed that this catalyst offered the possibility of obtaining various alkyl-substituted phenols as well as phenol ethers. The alkylation proceeds according to the following scheme:



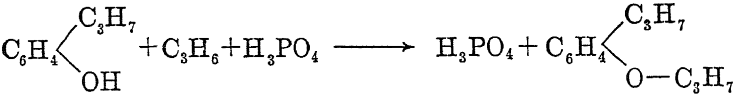
$$C_3H_6 + H_3PO_4 \longrightarrow O{=}P\begin{array}{l}\diagup OC_3H_7\\ -OH\\ \diagdown OH\end{array}$$

$$O{=}P\begin{array}{l}\diagup\\ -OH\\ \diagdown OH\end{array} + C_6H_5OH \longrightarrow C_6H_4\begin{array}{l}\diagup C_3H_7\\ \\ \diagdown OH\end{array} + H_3PO_4$$

Alkylation is the principal reaction, but the formation of phenyl ether also takes place:

$$C_6H_5OH + C_3H_6 + H_3PO_4 \rightarrow C_6H_5{-}O{-}C_3H_7 + H_3PO_4$$

In addition to this ether, the ether of an alkylated phenol may also be obtained:



$$C_6H_4\begin{array}{l}\diagup C_3H_7\\ \\ \diagdown OH\end{array} + C_3H_6 + H_3PO_4 \longrightarrow H_3PO_4 + C_6H_4\begin{array}{l}\diagup C_3H_7\\ \\ \diagdown O{-}C_3H_7\end{array}$$

Usually, a small amount of this ether is obtained, but its separation from the alkylated phenol by means of sodium hydroxide presents no difficulty.

Alkylation in the presence of phosphoric acid is also successful with naphthols. These experiments were carried out by Komarewsky, using a high pressure apparatus.

The alkylation of phenols by olefins with phosphoric acid as catalyst proceeds with such ease that even olefins diluted with other hydrocarbons may be used for this purpose.

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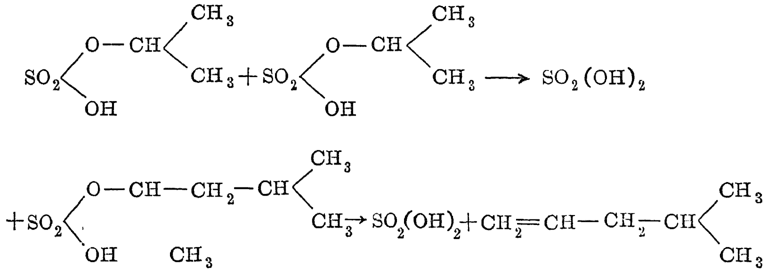
[1] Koenigs, Ber., *23*, 3145 (1890).

Thus, it is seen that the hypothesis proposed as the explanation of polymerization and dehydration is also applicable to alkylation.

The fact that polymerization and alkylation, when catalyzed by a hydroxylic acid, can be explained by the same mechanism, suggests the possibility of considering polymerization as a special type of alkylation. When ethyl benzene is obtained from benzene and ethylene, the reaction is described as the substitution of a hydrogen atom in the benzene nucleus by an ethyl radical, but actually this reaction is a condensation of two different hydrocarbon molecules. In polymerization reactions a hydrogen atom in the olefin is substituted by a hydrocarbon radical. Thus, for example, the hexylene produced by the polymerization of propylene may be considered as propylene with one of its hydrogen atoms substituted by the isopropyl radical:



Polymerization consists in the combination of like molecules of olefin to form one molecule of a hydrocarbon having a molecular weight which is a multiple of that of the original olefin. Alkylation consists in the combination of unlike hydrocarbon molecules to form one molecule of a hydrocarbon possessing chemical properties not identical with those of the starting hydrocarbons and having a molecular weight equal to the sum of the molecular weights of the original hydrocarbons.

POLYMERIZATION AND ALKYLATION UNDER THE INFLUENCE OF METAL HALIDES

The polymerization of ethylene in the presence of aluminum chloride was first studied by Ipatieff and Routala [1] under pressure at ordinary temperature. It was found that the lower boiling fractions of the product contained a certain amount of saturated hydrocarbons and that the higher fractions contained naphthenes (unsaturated hydrocarbons were removed by sulphuric acid).

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[1] Ipatieff and Routala, Ber., *46*, 1748 (1913); J. Russ. Phys. Chem. Soc., *45*, 995 (1913); C.A., *7*, 3972 (1913).

Stanley, Nash, and Bowen[1] repeated this work on a larger scale, confirmed the presence of saturated hydrocarbons in the upper (free) layer, and established the presence of more unsaturated hydrocarbons, $C_nH_{2n-2} \cdots C_nH_{2n-10}$, as well as olefins, in the lower layer. These investigators considered that the polymerization products obtained from ethylene resulted from a number of reactions. It is to be regretted that they carried out the polymerization of ethylene in the presence of straight run gasoline. As will be seen from our investigations, it cannot be assumed that all their products were formed from ethylene, there being a possibility that the gasoline hydrocarbons also reacted with olefins in the presence of the aluminum chloride.

Besides this polymerization reaction, the action of aluminum chloride as a catalyst for the alkylation of benzene by olefins was likewise known. It had been shown that it was possible to add ethylene, propylene, and other hydrocarbons to benzene to form alkyl benzenes. To ensure the success of this reaction, the presence of hydrogen chloride is necessary. This reaction has much in common with the well-known Friedel and Crafts reaction which consists in the alkylation of benzene by alkyl halides in the presence of aluminum chloride. Gustavson,[2] studying this reaction in the presence of aluminum bromide, assumed that reactions of the Friedel and Crafts type took place under the catalytic influence of a complex aluminum bromide compound $AlBr_3 \cdot 3C_6H_3(C_2H_5)_3$.

Our first study[3] in this series was on the alkylation of saturated hydrocarbons and naphthenes by olefins in the presence of aluminum chloride, zirconium chloride, and other halides. It was found that isobutane and higher paraffins can be alkylated by ethylene in the presence of aluminum chloride at atmospheric or superatmospheric pressure to give substituted paraffins:

$$C_6H_{14} + C_2H_4 \rightarrow C_8H_{18}$$

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[1] Stanley, J. Soc. Chem. Ind., 1930, 342. Nash, in his paper "On the Polymerization of Ethylene" pointed out that aluminum chloride does not act upon petroleum ether when ethylene is introduced into the latter, but the results of our experiments showed the contrary.

[2] Gustavson, Zentr., *14*, 344 (1883).

[3] I discovered that hexane can be alkylated by ethylene in the presence of aluminum chloride at ordinary pressure and low temperature (50–60°). It was also found that other types of hydrocarbons could be alkylated. The alkylation of paraffins was studied by Grosse and that of naphthenes by Komarewsky.

$$C_8H_{18} + C_2H_4 \rightarrow C_{10}H_{22}$$

$$C_6H_{14} + 2C_2H_4 \rightarrow C_{10}H_{22}$$

Examination of the product obtained by the alkylation of paraffins showed that practically the whole product consisted of hydrocarbons of the formula C_nH_{2n+2}. These hydrocarbons constituted the upper colorless layer and distilled up to 225°. There was a small lower layer which on decomposing with water yielded a high boiling oil consisting almost entirely of unsaturated hydrocarbons; the composition of the lower layer has not yet been fully determined.

Naphthenes such as cyclohexane and others are alkylated by ethylene in the presence of aluminum chloride at ordinary pressure forming substituted naphthenes:

$$C_6H_{12} + C_2H_4 \rightarrow C_8H_{16}$$

$$C_6H_{12} + 2C_2H_4 \rightarrow C_{10}H_{20}$$

The product boiling up to 225° which was obtained by the interaction of cyclohexane and ethylene consisted of substituted cyclohexanes as shown by the analytical data. The lower layer contained a very small amount of unsaturated hydrocarbons.

When propylene is used instead of ethylene, the polymerization reaction proceeds at a much higher velocity than the alkylation reaction and a lower layer is obtained which consists almost entirely of unsaturated hydrocarbons.

In all these experiments, the amount of aluminum chloride used was about 10% by weight of the hydrocarbon (together with a very little hydrogen chloride) and it is safe to assume that its action is catalytic. The falling off in activity of the catalyst may be due to side reactions. This point will be investigated in the future.

Comparing the reactions of polymerization and alkylation in the presence of aluminum chloride, it is to be concluded that in both cases there are several reactions taking place simultaneously. The explanation of the catalytic activity of aluminum chloride is to be found in its chemical properties, i.e., its ability to form complex addition compounds. These complexes, being unstable, decompose with regeneration of the catalyst, and the radicals thus liberated yield condensation products, e.g., they may become alkylated or they may produce polymers. The behavior of aluminum chloride is analogous to that of catalysts containing the hydroxyl group. In the latter case the participation of a certain amount of water is necessary in order for the reaction to proceed, and in the case of aluminum chloride it is necessary that a certain amount of hydrogen chloride be present.

In the polymerization of olefins, it is assumed that the olefin forms a complex compound with aluminum chloride and that two molecules of the complex decompose with liberation of olefins *in statu nascendi* which readily condense:

$$AlCl_2(CH_2{-}CH_2)Cl + AlCl_2(CH_2{-}CH_2)Cl \rightarrow 2AlCl_3 + CH_3{-}CH_2{-}CH{=}CH_2$$

$$AlCl_2(C_4H_8)Cl + AlCl_2(C_4H_8)Cl \rightarrow 2AlCl_3 + C_8H_{16}, \text{ etc.}^1$$

The growth of the chain, through the formation of complexes of increasingly higher molecular weight, occurs very rapidly until a hydrocarbon results which is no longer able to form a complex. It was noted that the addition of hydrogen chloride markedly increases the reaction velocity and also changes the character of the reaction.

It may be assumed that the complex combines with additional molecules of olefin and that the hydrocarbon chain grows in the complex itself. Therefore, it is difficult to understand the presence of olefins of various molecular weights in the reaction product.

It is possible that the hydrogen chloride reacts with the olefin and that the alkyl halide thus formed reacts with the hydrocarbon. Or it may be that the aluminum chloride forms an unstable complex with the hydrogen chloride (cf. BF_3HF, AlF_3HF) which on decomposing liberates an activated form of aluminum chloride which readily forms complexes with hydrocarbons.

Together with Grosse, I examined the action of hydrogen chloride on aluminum chloride under pressure but did not observe any absorption. It is possible that such a complex can be formed at low temperature but is incapable of existence, except in traces, at higher temperatures. This point will receive further study in the future.

It is seen that the first mechanism proposed by us has great possibilities. If we consider a polymerization reaction with phosphoric acid, using for example, propylene at a temperature of 100–

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[1] This complex could be written in another way, namely, $(CH_2ClCH_2)AlCl_2$, similar to the known compound $(CHCl{=}CH)HgCl$ formed by the action of acetylene upon mercuric chloride, but in the text the simpler formula is used.

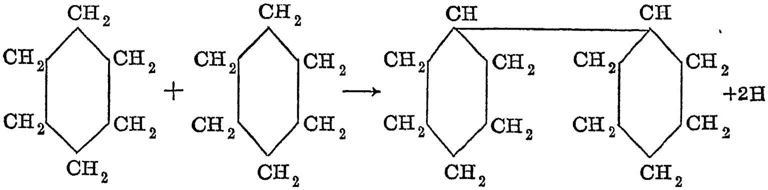
125°, we shall obtain a small amount of hexylene and a considerable amount of nonylene and dodecylene, but no paraffins or naphthenes. The reaction proceeds through the complex ester of phosphoric acid in such a way that two molecules of propylene gives hexylene, (1), which becomes alkylated in similar manner by propylene into nonylene, (2), the latter forming dodecylene, (3), and finally, two molecules of hexylene may directly condense to form dodecylene, (4).

$$(1)\ C_3H_6 + C_3H_6 \rightarrow C_6H_{12} \qquad (3)\ C_9H_{18} + C_3H_6 \rightarrow C_{12}H_{24}$$

$$(2)\ C_6H_{12} + C_3H_6 \rightarrow C_9H_{18} \qquad (4)\ C_6H_{12} + C_6H_{12} \rightarrow C_{12}H_{24}$$

The speed of polymer formation depends upon the ease of formation of esters of phosphoric acid. The polymerization of a mixture of propylene and isobutylene serves as proof of this assertion. Because the polymerization of isobutylene proceeds more readily than that of propylene, i.e., its velocity of ester formation is higher, then diisobutylene and triisobutylene should be present in the polymerization product and the propylene should give more hexylene and less nonylene and dodecylene under these conditions than it does when present alone. An experiment carried out with a mixture of these olefins gave a polymerization product whose distillation curve (Podbielniak) confirmed this assumption.

Regarding the formation of paraffinic hydrocarbons in the upper layer, it was finally established that naphthenic hydrocarbons readily alkylate each other under the influence of aluminum chloride with liberation of hydrogen.[1] This solves the question as to the mechanism of paraffin formation. The hydrogen liberated during the formation of high molecular polycyclic naphthenes hydrogenates the olefin —$AlCl_3$ complex and paraffins result.



$$AlCl_2(C_6H_{12})Cl + H \cdot H \rightarrow AlCl_3 + C_6H_{14}$$

The formation of a part of the paraffins may also be explained by the condensation of side chains split off from naphthenes. (See

[1] Ipatieff and Komarewsky, J. Am. Chem. Soc., *56*, 1926 (1934).

below regarding the formation of naphthenes.) The application of this scheme as explanation of the alkylation of paraffins and naphthenes by olefins in the presence of aluminum chloride is completely analogous. Aluminum chloride forms complex compounds with hydrocarbons which involves a type of chlorination.

$$\underset{\text{hexane}}{C_6H_{14}} \cdot AlCl_3 \rightarrow AlCl_2(C_6H_{13})HCl$$

$$\underset{\text{cyclohexane}}{C_6H_{12}} + AlCl_3 \cdot \cdot AlCl_2(C_6H_{11})HCl$$

The action of ethylene upon such a complex results in its decomposition with the formation of an alkyl substituted paraffin or naphthene.

$$AlCl_2[C_6H_{13}]HCl + C_2H_4 \rightarrow AlCl_3 + C_8H_{18}$$

$$AlCl_2[C_6H_{11}]HCl + C_2H_4 \rightarrow AlCl_3 + C_6H_{11}C_2H_5$$

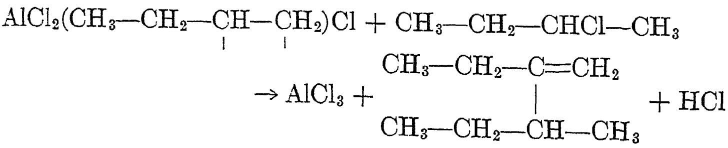
It is possible that not only does ethylene act upon this complex but also ethyl chloride, which is formed by the addition of hydrogen chloride to ethylene.

$$AlCl_2(C_6H_{13})HCl + C_2H_5Cl \rightarrow AlCl_3 + HCl + C_8H_{18}$$

The purpose of adding hydrogen chloride is to assist in the formation of complexes.

During alkylation reactions there is always a certain amount of polymer formation, the greater part of the unsaturated compounds appearing in the lower layer; this is an independent reaction.

The formation of naphthenes, either by polymerization or alkylation, may be explained by means of aluminum chloride complexes. For example, in the polymerization of butylene in the presence of aluminum chloride and hydrogen chloride, the following transformations take place:



$$AlCl_2(CH_3—CH_2—\underset{|}{C}H—\underset{|}{C}H_2)Cl + CH_3—CH_2—CHCl—CH_3$$
$$\rightarrow AlCl_3 + \begin{array}{l} CH_3—CH_2—C{=}CH_2 \\ \qquad\qquad\quad | \\ CH_3—CH_2—CH—CH_3 \end{array} + HCl$$

If this hydrocarbon decomposes into a saturated and an unsaturated compound, we will have a hydrocarbon with two double bonds which, as shown by my observation with allenes,[1] and particularly by Lebedeff's [1] investigation, polymerizes into cyclic hydrocarbons with great ease.

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[1] Ipatieff, J. prakt. Chem., *53*, 145 (1896); *59*, 517 (1899).

$$C_8H_{16} \rightarrow C_3H_8 + C_5H_8 \quad \text{or} \quad C_8H_{16} \rightarrow C_2H_6 + C_6H_{10}$$

This mechanism is capable of explaining the formation of a great variety of types of hydrocarbons as the result of alkylation. The Friedel and Crafts reaction in the alkylation of aromatic hydrocarbons may also be explained by the formation of the same complex between benzene and aluminum chloride; and halogenation may also take place according to the same scheme.

$$AlCl_2(C_6H_5)HCl + CH_3Cl \rightarrow C_6H_5CH_3 + AlCl_3 + HCl$$
$$AlCl_2(C_6H_5)HCl + Cl_2 \rightarrow C_6H_5Cl + AlCl_3 + HCl$$

Destructive Alkylation

Aluminum chloride, on the one hand, is capable of alkylating all classes of hydrocarbons with olefins and, on the other hand, it is able to decompose high molecular weight hydrocarbons. It would be interesting to study the decomposition of representatives of all classes of hydrocarbons, as well as the mutual action between the various classes of hydrocarbons in the presence of aluminum chloride. There are no accurate data in the literature sufficient for an analysis of these phenomena, but it is known that a hydrocarbon fraction of definite boiling range can be cracked in the presence of aluminum chloride so as to obtain hydrocarbons boiling both above and below the original cut. Experiments made with Grosse on the decomposition of hexane in the presence of aluminum chloride gave a decomposition product distilling over a wide range, the higher fractions boiling around 200°.

When hexane is subjected to decomposition at high temperature in the presence of alumina,[2] the product contains gas and also liquid which boils above the original hexane. It may be concluded that aluminum chloride splits the molecule of hexane into saturated and unsaturated molecules and brings about the alkylation of undecomposed hexane with olefins *in statu nascendi.* This would result in a growth of radicals upon the hexane skeleton.

$$C_6H_{14} \rightarrow C_4H_{10} + C_2H_4$$
$$C_6H_{14} + C_2H_4 \rightarrow C_6H_{13}C_2H_5$$

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[1] Lebedeff, Russ. Phys. Chem. Soc., *43*, 320–334 (1911).

[2] Ipatieff and Dovgelewitch, Ber., *44*, 2987 (1911).

A very small part of the resulting ethylene polymerizes under the influence of aluminum chloride, forming the higher olefins and diolefins found in the lower layer.

Of course, the ease of decomposition of the saturated hydrocarbon molecule into olefin and saturated hydrocarbon depends to a great extent upon the structure of the hydrocarbon. Isooctane, $(CH_3)_3CCH_2CH(CH_3)_2$, obtained by the reduction of diisobutylene is split by aluminum chloride at ordinary temperature, giving a series of hydrocarbons.

These experiments suggest decomposing various hydrocarbons in the presence of hydrocarbons which are not decomposed under the conditions of the experiment and which would be alkylated by the olefins resulting from the decomposition. Experiments made with Grosse on isooctane and benzene confirmed our assumption. Isooctane readily decomposed into isobutylene and isobutane:

$$(CH_3)_3C{-}CH_2{-}CH(CH_3)_2 \rightarrow (CH_3)_2C{=}CH_2 + CH_3{-}CH(CH_3)_2$$

and the isobutylene reacted with benzene in the presence of aluminum chloride to form tertiary butylbenzene in quantitative yield.

$$AlCl_2(C_6H_5)HCl + (CH_3)_2C{=}CH_2 \rightarrow AlCl_3 + C_6H_5{-}C(CH_3)_3$$

Experiments made with Komarewsky on more stable hydrocarbons such as pentane, hexane, and naphthenes, in the presence of benzene, as well as experiments with mixtures of naphthenes and paraffins, indicated that alkylation proceeds by virtue of the olefins formed by decomposition. Thus, hexane gave with benzene in the presence of aluminum chloride a 40–50% yield of ethyl benzene as shown by bromination and oxidation.

$$CH_3{-}CH_2{-}CH_2{-}CH_2{-}\vdots CH_2{-}CH_3 \rightarrow C_4H_8 + CH_2{=}CH_2$$

$$AlCl_2(C_6H_5)HCl + CH_2{=}CH_2 \rightarrow AlCl_3 + C_6H_5C_2H_5$$

Due to the fact that alkylation takes place after the hydrocarbon molecule has been decomposed, this process should be considered as *destructive alkylation.* But if the decomposed hydrocarbon alkylates itself, this process should be considered as *auto-destructive alkylation.*

This is only the beginning of our work. Our efforts are at present directed toward a study of the details of this reaction, applying it to other classes of organic compounds, as well as to the determination of the structure of certain hydrocarbons by subjecting them to decomposition in such a way that the radicals formed by decomposition unite with other hydrocarbons.

We have established the fact that other catalysts can also function as agents in alkylation. Phosphoric acid, as shown by Komarewsky, Pines, and myself, causes destructive alkylation, ethyl benzene being obtained from hexane and benzene. Experiments with Grosse with zirconium chloride at higher temperatures showed that this catalyst promotes both polymerization and destructive alkylation.

It is interesting to compare the explanations given in the case of different catalysts for the reactions of polymerization, simple alkylation, and destructive alkylation. Without doubt, these comparisons of the action of various catalysts assist us in understanding, from a chemical viewpoint, the nature of these processes. Our data make it possible to classify catalysts according to their chemical properties and their catalytic effects.

CHAPTER XI

POLYMERIZATION

POLYMERIZATION OF OLEFINS IN THE PRESENCE OF CATALYSTS

The conversion of gaseous olefins into higher homologs by polymerization received very little study prior to the present century. This lack of investigation may have been due, (1) to the difficulties encountered in studying the polymerization products (which consist of complex mixtures of hydrocarbons of various classes) or (2) because of the absence of practical interest. Moreover, it should be noted that in the beginning of the study of polymerization of olefins the products were obtained in very small amounts and the study of the properties of the resulting substances was therefore extremely difficult.

Butlerow and Gorianov [1] polymerized isobutylene in the presence of sulphuric acid; later, they used boron fluoride as a catalyst. With regard to the first member in the olefin series, ethylene, the literature contains no data describing the conditions under which its polymerization takes place. From experiments carried out by Berthelot,[2] Day,[3] and Norton and Noyes,[4] there are indications that ethylene decomposes rather than polymerizes under ordinary pressure at 450–500° and that liquid products are formed in such small amounts that it is impossible to obtain even an approximate determination of their character.

Ipatieff [5] repeated Day's experiments at a higher temperature (about 600°) and obtained only a few drops of liquid and detected the presence of saturated hydrocarbons in the residual gas.

Only by studying the influence of pressure upon the course of the catalytic decomposition of alcohols was Ipatieff able to prove that ethylene, when pumped into a high pressure apparatus and heated up to 360–400°, undergoes rapid polymerization whereby it is converted almost completely into a liquid containing hydrocarbons of various classes.

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[1] Butlerow and Gorianov, Ann., *169*, 143 (1873).

[2] Berthelot, Compt. rend., *50*, 805 (1860); *66*, 624 (1868); Ann. chim. phys., (3), *67*, 52 (1863); (4), *9*, 442 (1866); (4), *16*, 144 (1869); (5), *30*, 539 (1883); Bull. soc. chim., (2), *5*, 405 (1866); (2), *9*, 457 (1868).

[3] Day, Am. Chem. J., *8*, 153 (1886).

[4] Norton and Noyes, Am. Chem. J., *8*, 362 (1886).

[5] Ipatieff, J. Russ. Phys. Chem. Soc., *38*, 63 (1906); Zentr., 1906, II, 86.

He showed that pressure in the absence of catalysts is able to bring about the polymerization of olefins at certain temperatures. Regarding the action of catalysts upon the polymerization of olefins, Ipatieff proved in 1911–1913 that alumina, zinc chloride, and aluminum chloride considerably decreased the temperature necessary for the polymerization of olefins under pressure. Many years later, Ricard and Allenet (1922–1930), Szayna (1928–1929), Stanley (1930), Hurd, and others continued the study of aluminum chloride as catalyst for the polymerization of olefins for the purpose of obtaining lubricating oils. At that time Ipatieff did not attempt to explain the mechanism of the course of the reaction, either in the absence or in the presence of catalysts. But certain suggestions proposed by Ipatieff as to the possibility of converting ethylene into cyclohexane served as a basis for the first hypothesis attempting to explain the course of the polymerization process.

The study of the decomposition of cyclohexane under pressure in the presence of alumina, which indicated that various hydrocarbons are formed by the decomposition of naphthenes, was continued by Ipatieff and Dovgelevitch. From Ipatieff's early work on polymerization and that of other investigators, much of which appeared in the form of patents, it is not possible to formulate a mechanism for the process of polymerization. But the later investigations of Ipatieff and his co-workers, Pines, Corson, Schaad, White, Grosse, and Komarewsky on the polymerization of olefins with and without pressure, both in the presence and in the absence of catalysts, permit an approach to the understanding of this reaction and make possible the formulation of an hypothesis for the majority of the cases under consideration.

The following section is devoted to the description of experiments on the polymerization of olefins in the presence of different types of catalysts and the chapter on the "Theoretical Principles for Catalytic Reactions" presents an hypothesis on the mechanism of polymerization. This hypothesis permits the prediction of new polymerization catalysts for the lengthening of hydrocarbon chains of the olefin type.

POLYMERIZATION OF ETHYLENE

Many experiments were made in order to accumulate data and to study more thoroughly the character of the products obtained by the non-catalytic polymerization of ethylene under pressure.

For each experiment, about 30 liters of ethylene was compressed into an electrically heated high pressure apparatus containing an iron tube, the initial pressure being about 70 atmospheres. The experiments showed that appreciable polymerization of ethylene begins at about 325°; continues steadily at 350°, and at 380–400°, proceeds with such velocity that the pressure decreases 5 atmospheres per minute. Tables and graphs portraying this decrease in pressure with time were presented in preceding pages.

Heating of the apparatus was discontinued as soon as the pressure had practically ceased falling. Usually the final pressure in the apparatus after cooling was 20 to 25 atmospheres. On an average, the gases remaining after polymerization contained 52.8% of olefins, 4.2% of hydrogen, and 43% of paraffins.

Each experiment yielded 40 to 50 g. of liquid hydrocarbons. While a total of 1400 g. of a brownish liquid with a greenish cast was produced in a number of experiments, only an insignificant amount of solid products was formed.

The following fractions were separated in the first distillation of 1000 g. of the liquid product.

TABLE 131

FRACTION NO.	BOILING RANGE, ° C.	AMOUNT, G.
1	24–100	212
2	100–150	160
3	150–200	178
4	200–250	173
5	250–280	102
6	Over 280	210

All fractions reacted with bromine, decolorized potassium permanganate solution, dissolved partially in concentrated sulphuric acid, and oxidized on exposure to air with the development of a yellow color. Bromine and sulphuric acid were used to separate double bonded hydrocarbons from other hydrocarbons; for the first fraction sulphuric acid with a specific gravity of 1.84 was used; for the remaining fractions, 10% fuming sulphuric acid.

Prior to the removal of unsaturated hydrocarbons, the first fraction was redistilled and separated into the following fractions: (1) 22–30°; (2) 30–45°; (3) 45–60°; (4) 60–70°; (5) 70–80°; (6) 80–90°; (7) 90–108°. As seen below, the analyses of these fractions showed that they contained considerable amounts of both saturated and unsaturated hydrocarbons.

TABLE 132

Fraction No.	d_4^{20}	n_D^{20}	Analysis, Found	
			% C	% H
5	0.6857	1.39196	83.9	15.3
6	0.6950	1.39491	84.8	15.3
7	0.7017	1.40353	84.7	15.2
Calcd. for C_nH_{2n}			85.7	14.3

The fraction boiling from 60 to 100° contained about 50% of saturated hydrocarbons.

In order to remove olefins, the first four fractions were shaken with bromine in the cold until the appearance of a yellow color. The residual hydrocarbons from the first two fractions, which did not react with bromine, boiled at 30–37°; d_4^{20}, 0.6503; n_D^{20}, 1.36794. According to properties and analysis, these hydrocarbons consisted principally of pentanes.

Anal. Calcd. for C_5H_{12}: C, 83.3; H, 16.7. Found: C, 82.9; H, 16.4.

The hydrocarbons remaining from fractions 3 and 4, which did not combine with bromine (b.p., 60–66°; d_4^{20}, 0.6646) did not react with potassium permanganate solution or with nitrating mixture, and therefore consisted principally of hexanes.

Anal. Calcd. for C_6H_{14}: C, 83.7; H, 16.3. Found: C, 83.5; H, 16.0.

The hydrocarbons which combined with bromine were amylenes and hexylenes, but their structures were not determined because of insufficient material.

Of 200 cc. of the first fraction boiling at 24–100°, about 120 cc. was insoluble in 1.84 sulphuric acid. After washing with water and drying, the product distilled chiefly between 24 and 130°; d_4^{20}, 0.6481; n_D^{20}, 1.35652. It did not react with nitrating mixture or with potassium permanganate solution. The fact that there was no reaction with nitrating mixture indicated the absence of benzene hydrocarbons in this fraction of the polymerization products of ethylene, since this reaction is a sensitive test for these hydrocarbons.

Anal. Found: C, 84.2; H, 15.6.

The above analysis proved that this fraction did not consist wholly of paraffin hydrocarbons, but contained cycloparaffin hydrocarbons as well.

In order to test for the presence of naphthenes, the product remaining after treatment of the fraction boiling at 24–100° with 1.84 sp. gr. sulphuric acid was subjected to repeated distillation. In this way two fractions were separated.

TABLE 133

Fraction No.	B.P., ° C.	d_4^{20}	Analysis, Found	
			% C	% H
1	70– 80	0.6733	83.1	16.2
2	105–128	0.7339	84.7	15.5

The fraction boiling at 70–80° consisted chiefly of hexane admixed with heptane. The fraction boiling at 105–128° contained naphthenes since its carbon content and specific gravity were appreciably higher than that required for octane boiling at 125°.

Considerable amounts of the second and following fractions were insoluble in 1.84 sp. gr. sulphuric acid. The higher the boiling range of the fraction, the greater the amount of hydrocarbon insoluble in the acid. These insoluble hydrocarbons did not dissolve in fuming sulphuric acid, neither did they react with nitrating mixtures nor with potassium permanganate solution. After many distillations a number of fractions separated.

TABLE 134

Fraction No.	B.P., ° C.	d_4^{20}	n_{20}^{D}	Analysis				
				Calcd.			Found	
				For	% C	% H	% C	% H
3	131–138	0.7389	1.40973	C_9H_{18}	85.7	14.3	85.0	15.2
4	148–154	0.7505	1.41695	C_9H_{20}	84.4	15.6	85.1	15.0

Fraction 3 contained a considerable amount of cyclononane boiling at 135–136°; d_{20}, 0.7652. In addition, it contained octane boiling at 125°; d_{20}, 0.700; and nonane boiling point 150°; d_{20}, 0.718.

The boiling point of fraction 4 was indicative of nonane, but its specific gravity was too high for the paraffin hydrocarbon. This fraction contained a considerable amount of naphthenes.

The analyses and properties of the other fraction are summarized in the following table. In studying this table it should be borne in mind that naphthenes (C_nH_{2n}) contain 85.7% of carbon and 14.3% of hydrogen.

TABLE 135

B.P., ° C.	d_4^{20}	n_D^{20}	Analysis, Found		Reaction Product [a]
			% C	% H	
159–164	0.7598	1.42188	85.0	14.7	Alpha-decanaphthene, b.p., 160–162° Beta-decanaphthene, b.p., 168–170°; d_{20}, 0.7929
181–187	0.7945	1.43096	85.9	14.2	Undecanaphthene, b.p., 179–181°; d_{20}, 0.8119
194–202	0.7972	1.43449	85.2	14.9	Dodecanaphthene, b.p., 197°; d_{20}, 0.8005
200–210	0.7934	1.4392	85.5	14.4	
225–241	0.8192	1.4475	86.2	13.0	Tetradecanaphthene, b.p., 240–241°; d_{20}, 0.839
240–250	0.8198	1.4502	86.0	14.0	Pentadecanaphthene, b.p., 240–246°; d_{20}, 0.8265
250–256	0.8216	1.45369	86.0	14.1	
270–290	0.8375	1.46049	86.0	13.9	
270–285	0.8364	1.45089	86.1	13.9	

[a] Data on these naphthenes were taken from Höfer's book "Petroleum and Its Derivatives"; naphtha and derivatives, from the works of Markonikow and Oglobin.

The last three fractions contained considerable amounts of naphthenes, but because of the increase in carbon and the decrease in hydrogen content, it was concluded that hydrocarbons less rich in hydrogen were also present. In all probability these hydrocarbons were polycyclic naphthenes.

The 21% of polymerization product distilling above 280° at ordinary pressure gave a fraction boiling at 212–240° at 40 mm. pressure. This fraction was a thick, yellow oil similar to lubricating oil and contained about 20% of hydrocarbons soluble in sulphuric acid (*d*, 1.84). That part of the oil insoluble in acid distilled under diminished pressure at the same temperature as the original fraction; d_4^{20}, 0.8498; n_D^{20}, 1.45609.

Anal. Calcd. for C_nH_{2n}: C, 85.7; H, 14.3. Found: C, 86.3; H, 13.7.

Polymerization of Ethylene in the Presence of Alumina.—Polymerization of ethylene was carried out in an iron tube in the presence of alumina (2–3 g.) at 375° under the conditions previously described. The total of 190 g. of liquid product obtained was distilled into the following fractions: (1) 95–100° (20 g.); (2) 100–180° (30 g.); (3) 180–280° (55 g.); (4) above 280° (85 g.).

The yield of high boiling products (b.p. above 280°) formed in the presence of alumina was double that obtained in the absence of catalyst at a slightly higher temperature.

Fraction 2 (b.p., 100–180°) before treatment with sulphuric acid had d_4^{20}, 0.7454; n_D^{20}, 1.40682.

Anal. Calcd. for C_nH_{2n}: C, 85.7; H, 14.3. Found: C, 85.6; H, 14.5.

Treatment with sulphuric acid showed that this fraction contained 50% of olefin hydrocarbons and organic analysis indicated that paraffin hydrocarbons were also present, as was also the case with the polymer formed from ethylene in the absence of alumina.

Sixty per cent of fraction 3 (b.p., 180–280°) was insoluble in 1.84 sp. gr. sulphuric acid.

The hydrocarbons remaining after treatment of fractions 2 and 3 with 1.84 sulphuric acid were separated into fractions boiling at 128–138° and 225–240°.

TABLE 136

B.P., ° C.	d_4^{20}	n_D^{20}	Analysis, %				
			Calculated			Found	
			For	C	H	C	H
128–138	0.7529	1.41013	C_9H_{18}	85.7	14.3	84.9	15.2
225–240	0.8089	1.43771	$C_{14}H_{28}$	85.7	14.3	85.7	14.3

The first fraction contained nonane; the second, tetradecanaphthene.

In general it may be concluded that although alumina has a certain influence upon the course of polymerization, the fractions of corresponding boiling points produced in the presence and the absence of alumina contain the same hydrocarbons.

Polymerization of Isobutylene.—Isobutylene, obtained by Ipatieff's method of catalytic dehydration of isobutyl alcohol in the presence of alumina, was polymerized under the same conditions as used with ethylene. The reaction proceeded at 380–390° in an iron tube, its course being identical with that for ethylene. The residual gas contained 10.8% of hydrogen, 69.6% of olefins, and 20.1% of paraffins.

The composite of 500 g. of yellowish liquid obtained from all the experiments was distilled into the following fractions:

TABLE 137

CTION No.	B.P., ° C.	G.
1	23–100	70
2	100–150	105
3	150–190	55
4	190–215	58
5	215–260	82
6	260–280	55
7	Over 280	60

In general, the character of the polymerization products of isobutylene is the same as that of ethylene; except that more olefins are present in the first two fractions of the isobutylene polymers. This difference may be attributed to the fact that isobutylene polymerizes readily into diisobutylene and triisobutylene. The fact that the portion of the isobutylene polymer which is insoluble in 1.84 sulphuric acid reacts with nitrating mixture may be explained in the same way. In order to remove olefinic hydrocarbons it was necessary to treat the remaining hydrocarbons with fuming sulphuric acid. This treatment was particularly necessary with the first fractions. The hydrocarbons remaining after the second acid treatment did not react with nitrating mixture.

Isobutylene polymer remaining after the second sulphuric acid treatment was separated into the fractions in Table 138.

The analytical data indicate that the isobutylene polymer contained considerable naphthenic hydrocarbons. It should be noted, however, that the hydrogen content of the higher fractions of the product was practically constant, which distinguishes them from the higher fractions of the ethylene product.

TABLE 138

B.P., ° C.	d_{20}^{20}	n_D^{20}	Analysis, Found	
			% C	% H
95–130	0.7134	1.3856	84.4	15.4
105–120	0.7236	1.3962	84.6	15.1
190–210	0.7982	1.4001	85.5	14.4
215–235	0.8083	1.4060	85.7	14.4
250–261	0.8234	1.4131	85.8	14.2
265–285	0.8271	1.4127	85.8	14.3
		Calcd. for C_nH_{2n}	85.7	14.3

Investigation of the polymerization products of ethylene, as well as those of isobutylene, leads to the conclusion that they consist of mixtures of paraffin, olefin, and naphthene hydrocarbons. Chiefly paraffins together with olefins are present in the fractions boiling below 100°. Naphthenes are predominant in the higher fractions, increasing with the boiling point of the fraction. However, this may be true only to a certain extent, because there are indications that the fractions boiling above 250° contain hydrocarbons less rich in hydrogen than the naphthenes. In all probability these are polycyclic naphthenes.

An explanation of the mechanism of the polymerization of ethylene under the influence of heat and of pressure would be interesting, but it should be noted that the study of this reaction presents great difficulties, for without pressure, polymerization does not occur. Special experiments showed that ethylene remains almost unchanged when passed slowly through an iron tube at about 500°. This temperature cannot be increased because the naphthenes, as well as the paraffins, are decomposed.

Since polymethylene hydrocarbons are the chief products of ethylene polymerization, it is possible that ethylene may form cyclohexane, and that its decomposition products, such as acetylene, may polymerize to benzene on heating.

It may be recalled that olefins are present in all fractions of the polymerization product of ethylene. Therefore, it may be assumed that these olefins are formed either by the polymerization of ethylene directly, or that they are the decomposition products of naphthenes. As evidence for the second assumption, experiments showed that olefins were present in a number of the fractions of the decompositive product of cyclohexane.

The formation of paraffin hydrocarbons of relatively low molecular weight during the polymerization of ethylene, may be explained either by the hydrogenation of olefins or of naphthenes with scission of the nucleus, or by the splitting of side chains from the naphthenes.

The olefins polymerize into substituted naphthenes just as substituted acetylenes polymerize to substituted benzenes.[1]

The formation of naphthene and paraffin hydrocarbons by the polymerization of simple olefins is of especial interest since it presents an opportunity to answer definitely certain questions related to the organic hypothesis of the origin of petroleum.

Polymerization of Ethylene at High Temperature and Pressure in the Presence of Catalysts [2]

In the preceding pages, experiments have been described on the polymerization of ethylene and isobutylene under pressure in the absence of catalysts. Only one experiment was made on the polymerization of ethylene in the presence of alumina and it was seen that the resulting polymerization product was in general the same as that obtained in the absence of this catalyst, except that the fraction boiling above 250° was considerably larger (almost double).

The investigation of the catalytic polymerization of ethylene was undertaken in order to determine the influence of two catalysts, zinc chloride and aluminum chloride. Aschan [3] had studied the condensation of ethylene in the presence of aluminum chloride at ordinary pressure but with negative results.

Our experiments showed that aluminum chloride is an energetic catalyst under pressure and that it is also capable of bringing about the polymerization of ethylene even at ordinary temperature.

Polymerization of Ethylene in the Presence of Zinc Chloride.—Into the high pressure apparatus was introduced 5–6 g. of dry zinc chloride and about 40 liters of ethylene (initial pressure 70 atmospheres). On heating, the polymerization of ethylene took place at 275° as evidenced by decrease in pressure. Fifteen experiments on the polymerization of ethylene were made in the same apparatus. The time of heating varied with the individual experiment but on the average the pressure became more or less constant at the end of 50–60 hours. It was observed that polymerization proceeded more rapidly in the first experiments than in later ones, in spite of the fact that the iron tube was thoroughly cleaned after each experiment.

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[1] Preliminary explanations of the polymerization of ethylene hydrocarbons are presented here because these ideas were proposed by Ipatieff in 1911 when he first investigated this reaction. On studying the reaction more thoroughly during the years 1932–1933 in connection with catalytic alkylation, Ipatieff had data at his disposal which permitted him to formulate a general hypothesis explaining these types of reactions, and to follow more closely the entire course of the polymerization process (refer to the chapter discussing the theory of this catalytic reaction).

[2] Ipatieff and Routala, Ber., *46*, 1748 (1913).

[3] Aschan, Ann., *324*, 23 (1902).

On the average, about 22 g. of liquid condensation product was obtained in each experiment. On cooling the apparatus, the pressure fell to 30–35 atmospheres: the residual gas consisted of 30% of hydrogen, 36% of olefins, and 61% of paraffins.

The liquid reaction product (320 g.) was a petroleum-like liquid, brown in color, with specific gravity of 0.7512 at 15°. On distilling 300 g., the initial boiling point was 20° and the following fractions were obtained:

TABLE 139

Fraction No.	B.P., ° C.	G.	Color
1	20– 50	30	
2	50–100	40	Colorless
3	100–150	32	
4	150–200	20	
5	200–250	35	Yellowish
6	260–300	26	

The thick dark bottoms, 39% of the total reaction product, were distilled under diminished pressure. Fractions boiling below 300° were redistilled and the following fractions were obtained:

TABLE 140

Fraction No.	B.P., ° C.	G.	d_4^{20}	n_D^{20}
1	20– 36	7	0.6380 at 15°	1.35624 at 15°
2	36– 50	10	0.6452 at 15°	1.36237 at 15°
3	50– 85	28	0.6698	1.37493
4	85–110	17	0.7003	1.39186
5	110–128	10	0.7222	1.40310
6	128–145	7	0.7389	1.41494
7	145–165	8	0.7624	1.42289
8	165–205	21	0.7966	1.44164
9	205–250	28	0.8415	1.47086
10	250–300	21	0.8706	1.48890

All fractions possessed a petroleum-like odor, decolorized potassium permanganate solution, and added bromine. The first three fractions showed only a slight reaction with nitrating mixture which could be explained by the fact that they consisted chiefly of paraffin hydrocarbons; the remaining fractions reacted energetically.

Carbon-hydrogen analysis of these fractions gave the following results:

TABLE 141

Fraction No.	B.P., ° C.	Analysis			Found	
		Subs. G.	CO_2 G.	H_2O G.	% C	% H
1	20– 36	0.0993	0.3035	0.1449	83.3	16.3
2	36– 50	0.1071	0.3285	0.1558	83.6	16.2
3	50– 85	0.1336	0.4116	0.1883	84.0	15.7
4	86–110	0.1132	0.3504	0.1240	84.4	15.3
5	110–128	0.0848	0.2640	0.1150	84.9	15.1
6	128–146	0.0915	0.2867	0.1203	85.5	14.6
7	145–165	0.1368	0.4278	0.1822	85.3	14.8
8	165–205	0.0985	0.3137	0.1088	87.4	12.3

The analyses indicate that the first fraction contained principally pentane; the second and third fractions, hexane; the higher fractions, hydrocarbons rich in carbon. All fractions, beginning with the third, were treated with concentrated sulphuric acid; the olefin content of the different fractions are presented in the following table:

TABLE 142

Fraction No.	B.P., ° C.	Olefins, %
3	50– 85	15
4	85–110	23
5	110–128	36
6	128–145	37
7	146–165	41
8	165–205	50
9	205–250	56
10	250–300	62

As seen from the above table, the olefin content of the polymer increases with the rise in boiling point. Correlating the boiling point, olefin content, and organic analytical data, it follows that the fractions boiling below 145° contained hexylene, heptylene, octylene, and nonylene as well as paraffin hydrocarbons. This conclusion follows from the data presented in the following table.

TABLE 143

Fraction No.	B.P., ° C.	d_4^{20}	n_D^{20}	Analysis, Found		Olefin Content, %
				% C	% H	
3	50– 85	0.6698	1.3749	84.0	15.7	15
4	85–110	0.7003	1.3918	84.4	15.3	23
5	110–128	0.7222	1.4031	84.8	15.1	36
6	128–145	0.7389	1.4149	85.5	14.7	37
Hexylene	68			85.7	14.3	
Heptylene	98	0.7030		85.7	14.3	
Octylene	124	0.7217	1.4157	85.7	14.3	
Nonylene	153	0.7433		85.7	14.3	

In order to separate the saturated hydrocarbons, the fractions boiling below 50° were treated with bromine in the cold. The liquid which did not react with bromine was fractionated and a fraction was separated which boiled at 29–41°. The properties of this fraction (d^{15}_{20}, 0.6239; n^{15}_D, 1.3511) justified the conclusion that it consisted chiefly of isopentane.

Anal. Calcd. for C_5H_{12}: C, 83.3; H, 16.7. Found: C, 82.8; H, 16.6.

Analysis and properties showed that methyltetramethylene (methylcyclobutane) was not contained in this fraction. Aschan [1] found this hydrocarbon in the polymer formed from amylene under the influence of aluminum chloride, but it was not formed by the action of zinc chloride. There is a possibility, because of the high temperature and the catalyst used, that isomerization of lower boiling naphthenes to olefins took place, as was proved by an experiment made by one of us.[2]

Concentrated and fuming sulphuric acid (containing 7 to 10% of anhydride) were used for removing unsaturated hydrocarbons. After treatment with sulphuric acid, all the fractions were distilled and the following fractions obtained: (1) I. B. P.–60°; (2) 60–63°; (3) 63–85°; (4) 85–110°; (5) 110–130°; (6) 130–156°; (7) 156–177°; (8) 177–200°; (9) 200–220°; (10) 220–243°; (11) 243–256°; (12) 256–265°.

The analyses and properties of these olefin-free fractions are summarized in the following table:

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[1] Aschan, Ann., *324*, 26 (1902).

[2] Ipatieff, Ber., *36*, 2014 (1903).

TABLE 144

B. P., °C.	d_{20}	n^{20}_D	ANALYSIS, FOUND					REACTION PRODUCT, ANALYSIS CALCD.
			Subs. G.	CO_2 G.	H_2O G.	% C	% H	
60– 63	0.6529	1.36764	0.1021	0.3126	0.1494	83.5	16.3	Hexane, C_6H_{14} C—83.7% H—16.3%
63– 85	0.6645	1.3727	0.0972	0.2977	0.1422	83.5	16.2	Hexane
85–110	0.6875	1.3850	0.1356	0.4173	0.1941	83.9	15.9	Heptane, C_7H_{16} C—84.0% H—16.0%
110–130	0.7085	1.3948	0.1109	0.3420	0.1575	84.1	15.8	Octane, C_8H_{18} C—84.2% H—15.8%
130–156	0.7304	1.4050	0.1240	0.3856	0.1687	84.8	15.1	Nonane Nonanaphthene Isodecanaphthene
156–177	0.7500	1.4148	0.1591	0.4956	0.2138	85.0	14.9	Decane Alpha-decanaphthene Beta-decanaphthene
177–200	0.7651	1.4216	0.1590	0.4972	0.2098	85.3	14.7	Undecane Undecanaphthene Dodecanaphthene
200–220	0.7833	1.4303	0.1211	0.3792	0.1585	85.4	14.5	Dodecane Tridecanaphthene
220–243	0.8041	1.4364	0.0894	0.2802	0.1166	85.5	14.5	Tetradecanaphthene Tridecane
243–256	0.8175	1.4467	0.1099	0.3456	0.1405	85.8	14.2	Pentadecanaphthene Tetradecane
256–265	0.8278	1.4495	0.1491	0.4698	0.1895	85.9	14.1	Naphthene C—85.7% H—14.3%

None of the fractions which were investigated reacted with nitrating mixture, neither did they decolorize potassium permanganate solution. Fractions 6 to 12, inclusive, consisted of polymethylene hydrocarbons, the amount of which increased with rise in boiling point. Fraction 12 consisted almost entirely of polymethylenes.

These results are comparable with those obtained by Ipatieff,[1] Engler,[2] and Routala[3] in which equal mixtures of hydrocarbons were obtained by the condensation of ethylene hydrocarbons in the absence of catalysts.

In the following diagram, the boiling points of the fractions are plotted as abscissae against the specific gravity values as ordinates.

Curve I has reference to products originating from amylene on standing in the presence of aluminum chloride at room temperature and atmospheric pressure. Curve II illustrates the change in specific gravities with change in boiling point of the naphthenes known at the present time. Curve III represents the yield of hydrocarbons of different boiling points obtained by the condensation of ethylene in the presence of zinc chloride.

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[1] Ipatieff, J. Russ. Phys. Chem. Soc., *43*, 1420 (1911).

[2] Engler, Ber., *42*, 4620 (1908).

[3] Routala, Dissertation, Karlsruhe (1909).

Curve IV is a plot of the yields of saturated products formed by the condensation of amylene under pressure. These results were obtained by Engler and Routala. A study of Curves I, III, and IV leads to the conclusion that they are typical of the composition of the principal types of petroleum:

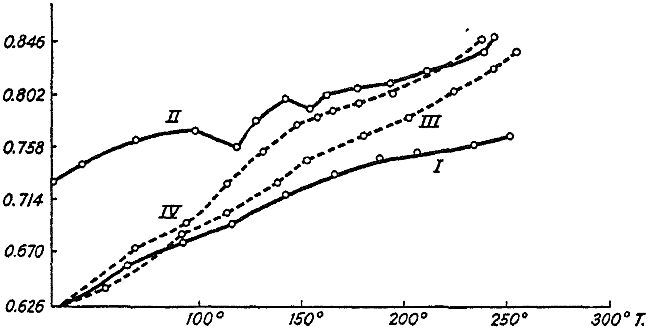

FIG. 35

TABLE 145

CURVE No.	TYPES OF PETROLEUM	REMARKS
I	American	Poor in naphthenes
III	Galician	Averages between I and IV
IV	Baku	Rich in naphthenes

Thus, by choosing suitable experimental conditions (temperature, pressure, and catalyst), all of the principal types of petroleum may be obtained artificially.

The fraction of ethylene polymer boiling above 280° (39% of the total liquid yield) was distilled under diminished pressure (7–10 mm.) and separated into the fractions shown in Table 146.

All fractions possessed an aromatic odor and reacted energetically with bromine. Increase in the boiling point of the fractions was accompanied by a darkening in color and increase in viscosity. Fractions 1 and 4 were identical in composition. The above analyses indicate that they consisted of mixtures of naphthene and olefin hydrocarbons. More than half of these fractions dissolved in fuming sulphuric acid leaving a colorless liquid (d_{20}, 0.8528; n_D^{20}, 1.4575) which did not react with nitrating mixture.

TABLE 146

Fraction No.	B.P., ° C. @ 7–10 Mm.	G.	d_{20}	n_D^{20}	Analysis, Found		Remarks
					% C	% H	
1	160–175	29	0.9034	1.5035	88.1	11.9	Yellow
2	175–190	25	0.9200				Dark yellow
3	190–230	21	0.9222				Dark reddish brown
4	230–263	26	0.9305		88.2	11.8	Dark brown

Anal. Calcd. for C_nH_{2n}: C, 85.7; H, 14.3. Found: C, 86.2; H, 13.7.

Polymerization of Ethylene in the Presence of Aluminum Chloride.—For the polymerization of ethylene in the presence of aluminum chloride, this gas was pumped into the high pressure apparatus to a pressure of seventy atmospheres at room temperature. An insignificant amount of liquid hydrocarbons was produced at 240°. At 280° the only products were a carbonaceous residue and a gas containing 10% of hydrogen, 4% of olefins, and 86% of paraffins. When freshly prepared aluminum chloride was employed, the ethylene polymerized to liquid products at ordinary temperature. No liquid products were obtained at 200° but a carbonaceous residue remained in the apparatus.

The polymerization product was a fluorescent, greenish-red liquid with a disagreeable odor; d_{15}, 0.7842. This liquid, about 30% of which boiled below 150°, was separated by distillation into the following fractions:

TABLE 147

Fraction No.	B.P., ° C.	G.	d_{20}	n_D^{20}
1	21–100	10	0.6777–15°	1.3690–15°
2	100–200	6	0.7302	1.4054
3	200–300	6	0.8013	1.4434
Above	300	9		

The first three fractions were treated with fuming sulphuric acid to remove unsaturated hydrocarbons. The olefin-free hydrocarbon was then distilled into four fractions, analyses and properties of which are tabulated in the following table.

TABLE 148

Fraction No.	B.P., ° C.	d_{20}	n_D^{20}	Analysis				
				Subs. G.	CO_2 G.	H_2O G.	% C	% H
1	31– 85	0.6574/15°	1.3645/15°	0.0971	0.2973	0.1424	85.5	16.3
2	85–156	0.6946	1.3884	0.0869	0.2691	0.1221	84.4	15.6
3	156–200	0.7344	1.4072	0.0791	0.2468	0.1089	84.7	15.2
4	200–250	0.7766	1.4260	0.0940	0.2936	0.1234	85.1	14.6

None of the fractions reacted with bromine, potassium permanganate solution, or nitrating mixture. According to analysis, the first three fractions consisted chiefly of paraffin hydrocarbons, while the fraction boiling above 280° contained naphthenes. According to these first experiments it may be concluded that less naphthenes are formed by the polymerization of ethylene in the presence of aluminum chloride than in the presence of zinc chloride.

Concerning the Question of the Origin of Petroleum [1]

Experiments on the polymerization of olefins, as well as on the decomposition of hexane and cyclohexane at high temperatures and pressures, and the earlier (1904) experiments of Ipatieff on the decomposition of organic compounds under pressure, induced me to study more closely the existing hypotheses on the origin of petroleum in nature, and to make additional experiments in order to clarify certain questions arising in this connection.

The mineral hypothesis of the origin of petroleum as first proposed by Berthelot and developed particularly by Mendeléeff was accepted by many chemists and geologists. The reason for this may be seen in the experiments of Hahn [2] and Cloez [3] who showed that treatment of certain kinds of cast iron with dilute hydrochloric acid and sea water produced a mixture of gaseous, liquid, and solid hydrocarbons with the formula C_nH_{2n} which distilled over a wide temperature range and it was evident that these hydrocarbons might serve as the basic material for the formation of petroleum.

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[1] Ipatieff, J. prakt. Chem., *84*, 800 (1911). This work is included in the chapter on Polymerization because the origin of petroleum is closely identified with this reaction; also, it is obvious that a study of these chemical reactions may be of assistance in explaining the complex processes occurring in the depths of the earth during geological ages.

[2] Hahn, Ann., *129*, 57 (1864).

[3] Cloez, Compt. rend., *78*, 1565 (1874).

According to Mendeléeff's hypothesis, petroleum is formed in rock folds by the action of water upon iron carbides which have migrated from the depths of the earth into the upper layers of sedimentary rock where they were laid down as a secondary deposit.

More recently, the so-called organic hypothesis of the origin of petroleum was formulated by Engler who, since 1888, has made many interesting experiments on the decomposition of fats and mollusks at high temperature (400°) under 25 atmospheres pressure. The decomposition of fats yielded various classes of hydrocarbons, considerable amounts of paraffins and olefins, and a relatively small amount of naphthenes. The gases contained about 30% of hydrogen and appreciable quantities of ethylene, carbon monoxide, and carbon dioxide. The quality and the quantity of the products derived from fatty substances were shown by Engler to depend to a great degree upon the experimental conditions. Engler attributed the absence of any but small amounts of nitrogen in petroleum to the rapid putrefaction of albumins in organisms whereby nitrogen is liberated in the form of free nitrogen, ammonia, or other complex nitrogen compounds, only insignificant amounts remaining in the petroleum. Soon after Engler published the results of his experiments, he attracted many followers, and today his "organic hypothesis" on the origin of petroleum receives wide recognition.

Here it is interesting to point out the reason why the organic hypothesis rapidly replaced the mineral hypothesis. Both hypotheses are based on chemical investigations. The organic hypothesis of Engler will first be discussed and the experimental data leading to its acceptance will be scrutinized. Regarding the experiments of Engler, there are serious disagreements in the composition of natural petroleum products as compared with that of the substances actually obtained by the decomposition of fats. Thus, for example, the formation of considerable amounts of carbon monoxide, as well as hydrogen, was objected to by Fr. Philips and others because the gaseous products obtained from the original sources of petroleum contain very small amounts of these gases. However, these and other objections did not prevent the organic hypothesis from replacing the mineral hypothesis. The reason for this replacement may be found in the fact that it is much more plausible from a geological standpoint than the mineral hypothesis.

It must be remembered that the organic hypothesis was acknowledged by many geologists even before Engler made his investigations, though chemists were inclined to accept the hypothesis of Mendeléeff. But after the experiments of Engler, Geissler, Aschan, and others, and after the discovery of the optical rotation of petroleum by Tschugaeff, Walden, and Rakusin, the great majority of chemists accepted the organic hypothesis. From a chemical standpoint, previous objections have no significance at present.

About eight years ago, I showed in my original investigations on the pyrolysis of organic substances that compounds containing oxygen (for example, alcohols and aldehydes) decompose at high temperature and pressure chiefly into paraffin hydrocarbons, water, and small amounts of carbon dioxide and ethylene; carbon monoxide and hydrogen being formed in very small amounts. The higher the pressure, the smaller the amounts of carbon monoxide and hydrogen formed and the greater the production of hydrocarbons. The ethylene undergoes polymerization with conversion into a series of hydrocarbons as discussed previously. It must be emphasized, however, that no carbon residue is formed by the decomposition of organic compounds under high pressure but that such a residue forms in decomposition at ordinary pressure.

The following gas analyses are tabulated to show that the decomposition under pressure of organic compounds containing oxygen produces gases similar in composition to those liberated from petroleum.

TABLE 149

Source of Gas	Composition, % by Volume				
	Carbon Dioxide	Carbon Monoxide	Hydrogen	Paraffins	Olefins
Alcohol Decomposition	6.2	4.0	13.2	71.0	5.6
Surachan Petroleum Pits	4.5	2.2		92.3	0.9

Thus, considering the influence of time, temperature, pressure, and catalysts which previous experiments have shown are significant factors in the pyrolysis of organic compounds, the presence of various substances in petroleum, as well as the varying character of different types of petroleums present in the depth of the earth may be readily explained.

From the above discussion, it is obvious that the chemical investigations of Engler, the decompositions involved in pyrolysis under pressure as set forth by Ipatieff, and the work of other investigators confirm at present the fundamental ideas embodied in the organic hypothesis of the origin of petroleum, but further work should be undertaken in order to find the answer to such questions as the age of this or that type of petroleum, and the possibility of converting one type of petroleum into another.

On examining the hypothesis of Mendeléeff, it must be acknowledged that it is based upon the investigations of Hahn and Cloez who made their experiments at a time when the various classes of hydrocarbons had received but little study. In order to be convinced, in so far as the investigations of Hahn and Cloez may serve as a basis for the experiments of the mineral hypothesis, I decided to repeat the experiments of these investigators and to examine the products obtained by the action of dilute hydrochloric acid upon various kinds of cast iron.

The cast irons used for these experiments were manganese cast iron with 5% carbon content, white cast iron (from the foundry of Graf Stroganov), containing 4.5% of C, 0.31% of Si, 0.43% of Mn, 0.0% of S, 0.027% of P, and ordinary gray cast iron. Six hundred grams of iron filings was placed in a large round bottom flask and covered with hydrochloric acid (sp. gr., 1.19 diluted with 2 volumes of water). The flask was placed on a water bath at 80–90° and the products were passed through a condenser, two bottles filled with cold water, a Drexel flask containing copper sulphate solution, and finally through two bottles containing bromine water. The reaction was run continuously for one year during which time 70 kilos of cast iron was treated. Of this amount, about 50 kg. was manganese cast iron.

The liquid collected in the bottles filled with water was poured out from time to time and fresh water was substituted. After decolorization of the bromine water, the resulting bromides were removed and the flasks were refilled with fresh bromine water. About 180 g. of liquid hydrocarbons and approximately 1 kilo of bromides were obtained from the manganese cast iron. The white cast iron gave a smaller yield of hydrocarbons and was also more difficult to dissolve in the acid. Only a very small amount of liquid hydrocarbons was obtained from the gray cast iron; therefore, these hydrocarbons were not investigated individually. A similar observation for gray cast iron was made by Cloez. Less bromides were obtained from gray than from the white cast iron, but both samples of these bromides distilled at the same temperatures.

The gas obtained by dissolving cast iron, after passing through water, had the following average composition: olefins 4%, hydrogen 83.6%, paraffins 11.6%.

The bromides obtained from all three types of cast iron were distilled at ordinary and diminished pressure and separated into the following fractions:

At ordinary pressure:

(1) 129–132°
(2) 140–142°
(3) 151–154°

Under diminished pressure (30 mm.):

(4) 80–100°
(5) 100–130°
(6) 130–160°
(7) greater than 160°

The bromine contents of the first three fractions were as follows:

TABLE 150

Fraction	Found, % Br	Calculated	
		For	% Br
1	83.6	$C_2H_4Br_2$	85.1
2	78.3	$C_3H_6Br_2$	79.1
3	74.6	$C_4H_8Br_2$	74.1

According to the analyses and properties of the bromides obtained, it may be concluded that gaseous olefins such as ethylene, propylene, and butylene are formed by dissolving cast iron in hydrochloric acid.

The fraction boiling from 150 to 160° at ordinary pressure was separated from the fourth fraction and treated with zinc dust in alcoholic solution. The gaseous hydrocarbon evolvėd was butylene of normal structure; it did not give the crystalline nitrosylchloride characteristic of isobutylene. The remainder of the bromides of the fourth fraction, on treatment with zinc dust in alcoholic solution under a reflux condenser, gave a liquid hydrocarbon which was collected in a receiver cooled with snow and salt. This liquid distilled at 24–84°. It was separated into the following fractions: (1) 33–45° (21 g.); (2) 45–80° (20 g.).

The fraction boiling at 33–45° consisted of a mixture of pentenes; it dissolved completely in sulphuric acid.

The fraction boiling at 45–80° had d_{20} of 0.6849 and n_D^{20} of 1.37887. According to these properties and the following analysis, this fraction consisted of a mixture of hexylenes and heptylenes.

Anal. Calcd. for C_6H_{12}: C, 85.7; H, 14.3. Found: C, 85.6; H, 14.0.

The fraction which boiled from 100 to 130° at 30 mm., on treatment with zinc dust and alcohol, gave a mixture of hydrocarbons boiling at 84–114°; d_{20}, 0.7143; n_D^{20}, 1.39028. These properties and the analysis indicated the presence of octylenes.

Anal. Calcd. for C_nH_{2n}: C, 85.7; H, 14.3. Found: C, 85.3; H, 14.0.

The higher boiling bromide fractions were not treated with zinc dust and alcohol since they contained tri- and tetrabromides formed by the action of excess bromine upon the dibromides.

The liquid hydrocarbons from the manganese cast iron which were collected in the bottles filled with water, were dried and distilled. The following fractions were obtained from 100 g. of liquid: (1) 75–120° (6 g.); (2) 120–160° (30 g.); (3) 160–200° (40 g.); (4) 200–215° (13 g.). All fractions were colorless liquids which had the odor of olefins and which became yellow on long standing.

Properties and analyses of these fractions are presented in the following table:

TABLE 151

B.P., ° C.	d_{20}	n_D^{20}	Analysis, Found		Calculated for C_nH_{2n}	
			% C	% H	% C	% H
120–160	0.7510	1.4114	85.2	14.2	85.7	14.3
145–150	0.7300	1.3941	85.8	14.2		
160–200	0.7731	1.4225	85.6	14.2		
200–215	0.7958	1.4334	85.9	13.9		

From the analyses it is obvious that the liquid products obtained from the manganese cast iron were hydrocarbons of the formula C_nH_{2n} and that, according to their properties, they should be considered as mixtures of various olefins. All fractions decolorized potassium permanganate solution, reacted strongly with nitrating mixture, and dissolved almost completely in sulphuric acid (*d*, 1.84). In the higher boiling fractions there were small amounts of non-olefinic hydrocarbons.

Thus, by treating 20 cc. of the fraction boiling at 160–200°, first with strong sulphuric acid and then with fuming sulphuric acid (10% SO_3), about 2 cc. of liquid hydrocarbon remained insoluble which distilled at 170–190°, did not react with potassium permanganate solution, and only weakly with nitrating mixture.

Anal. Found: C, 85.2; H, 14.7.

The composition of this hydrocarbon corresponds closely to the formula C_nH_{2n}. Because of the absence of reactions characteristic of the ethylene bond, it is very probable that this hydrocarbon was a naphthene.

The products obtained by treating white cast iron with hydrochloric acid were identical in character with those obtained from the manganese cast iron.

In conclusion it may be said that the gas obtained by treating cast iron with dilute hydrochloric acid consisted of hydrogen together with small amounts of paraffins and olefins. On the other hand, the hydrocarbons generated from the bromides, as well as those obtained directly as liquid condensate, contained no paraffins, but consisted of olefins with slight admixture of naphthenes only in the higher fractions.

The question now arises as to whether this chemical investigation may be considered as sufficient confirmation of the hypothesis of the origin of petroleum from the decomposition of carbides by means of sea water. It must be recognized that the investigations of Hahn and Cloez which were made at ordinary pressure are insufficient to establish the mineral hypothesis principally because in this reaction only olefins are formed. My experiments on the polymerization of ethylene and of other olefins under the influence of heat, as well as pressure, showed that under these conditions olefins are able to form various hydrocarbons including naphthenes. These results confirm, from the chemical viewpoint, the mineral hypothesis of petroleum formation. Furthermore, if we take into consideration the possibility of catalytic action during the secondary processes which accompany the formation of petroleum, then all objections to the mineral hypothesis from the chemical standpoint will be completely removed.

But it has also been noted that the decomposition of various organic compounds and the polymerization of simple olefins occur at relatively low temperatures and this is evidence in favor of the organic hypothesis of the origin of petroleum. In spite of the fact that chemical investigation shows that the mineral hypotheses can explain the origin of petroleum, we are, nevertheless, inclined to acknowledge the validity of the organic hypothesis. The final proof must rest upon geological evidence.

All geological records show that primary deposits of petroleum are present only in those layers formerly supporting life and that migration of petroleum takes place only through those layers which it can penetrate. In such a case, there would be a secondary deposit. Geologists and biologists advance the theory of the submergence of plants and animals under the sea and depositions on sea coasts (still occurring in the inlet creek of Karabugas and in the Red Sea) and they offer the interesting observations of the geologist Andrussov on the formation of hydrogen sulphide in the Black Sea as a result of the submergence of animals. They consider that petroleum originated principally from animals although the participation of sea plants is not to be excluded.

Sabatier explained the formation of petroleum from acetylene and Vignon [1] showed that methane and ethylene are formed when water vapor is passed through carbon containing lime; therefore, it is possible to formulate a hypothesis on the origin of petroleum from these compounds. The natural production of methane is illustrated by the formation of marsh gas. According to the investigations of Ipatieff [2] on the polymerization of ethylene, it may also be assumed that petroleum originated from marsh gas under pressure and at high temperature.

Polymerization of Olefins under the Influence of Sulphuric Acid

Since the experiments of Butlerow [3] and also of Brooks, Humphrey, Gurvitch, Norris and Joubert, Ormandy and Craven, and Lebedev, it has been known that sulphuric acid can bring about the polymerization of olefins, especially those containing a tertiary carbon atom. However, many phases of this polymerization reaction have not been clear. The most interesting work on the clarification of the nature of polymerization is that of Ormandy and Craven [1] who showed that in the polymerization of amylene with sulphuric acid (sp. gr., 1.86), paraffins of high boiling point are obtained and not olefins as previously supposed. It is to be regretted that these investigators did not sufficiently test their results since their conclusions seem to be incorrect. Lebedew and Kobylanski [2] repeated the work of Butlerow on the polymerization of isobutylene using 5 parts by weight of sulphuric acid and 1 part by weight of water and showed that all the polymerization products were olefins of the formula C_nH_{2n}.

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[1] Vignon, Compt. rend., *152*, 871 (1911).

[2] Ipatieff, Ber., *44*, 2978 (1911).

[3] Butlerow and Gorgainow, Ber., *6*, 196 (1873).

Because of the contradictory data, Ipatieff and Pines (1931) studied the polymerization of olefins [3] under the influence of sulphuric acid of different concentrations, the main purpose being to determine the character of the hydrocarbons obtained in this reaction.

The action of sulphuric acid was first studied on a mixture of olefins with aromatic and naphthenic hydrocarbons, amylene (b.p., 35–38°) and octylene (b.p., 124°) being the olefins chosen.

Experiments were made in cylinders fitted with ground stoppers into which were poured 15 cc. of sulphuric acid and 10 cc. of the hydrocarbon mixture. The cylinders were immersed in ice water and shaken continuously, the volumes of the acid and hydrocarbon layers being read every 10 minutes.

A large number of experiments showed that it is impossible to separate and to determine olefins by sulphuric acid in the presence of aromatic hydrocarbons. Even the determination of olefins by sulphuric acid in the presence of paraffins and naphthenes must be done with great care, using an excess of sulphuric acid and a short contact time, since polymerized olefins, difficultly soluble in sulphuric acid (*d*, 1.86), separate on standing.

The hydrocarbon remaining after treatment with sulphuric acid in the presence or absence of aromatic hydrocarbons was subjected to various tests such as determination of refraction index, bromine number, nitration, and the action of potassium permanganate solution. From the results obtained, the following conclusions were drawn:

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[1] Ormandy and Craven, J. Inst. Petroleum Tech., *13*, 317 (1927); J. Am. Chem. Soc., *49*, 873 (1927).

[2] Lebedev and Kobylanski, Ber., *63*, 103 (1930).

[3] Grosse also took part in the first phases of the study.

(1) On the basis of numerous organic analyses and reactions with potassium permanganate solution and nitrating mixture, it was found that the low boiling fractions contained principally paraffins and that the high boiling fractions contained olefins.

(2) Alkylation of the benzene ring occurred. In the case of amylene, mono-, di-, and tri-amyl benzenes were obtained.

(3) The presence of paraffins and naphthenes does not interfere with the alkylation process.

(4) The alkylation velocity of benzene by olefins is greater than that of polymerization; alkylated benzenes are obtained which are very stable to potassium permanganate solution.

(5) The conclusions drawn by Ormandy and Craven concerning the presence of saturated hydrocarbons in the higher fractions as well as their conclusion that benzene condenses with the polymerization products of amylene are not completely in agreement with the facts.

These investigations indicate that careful consideration must be given to the nature of the hydrocarbons that are to be determined by sulphuric acid, particularly in the case of olefins in the presence of aromatics. Published data regarding the composition of hydrocarbons obtained by cracking and pyrolysis should be critically reviewed if sulphuric acid has been employed as the analytical reagent. In order to determine the nature of the various hydrocarbons obtained by the polymerization of olefins, an investigation of the polymerization of amylene was made.

Polymerization of Amylene

Amylene (Eastman Kodak Company; b.p., 34–37°) was used in the investigation. One volume of amylene was shaken at 0° with 1.5 volumes of 92% sulphuric acid. The shaking was cautious at first, and more energetic toward the end of the reaction. After complete solution of the amylene in sulphuric acid, the reaction product was allowed to stand 24 hours at 0°. Two layers formed, the upper layer being composed of polymers, the lower layer consisting of a solution of amyl esters of sulphuric acid in sulphuric acid. The upper layer, after washing with alkali and water, was dried with calcium chloride. The amount of polymers formed in the upper layer totaled about 75% of the amylene treated.

TABLE 152

Polymerization of Amylene by Sulphuric Acid

Expt. No.	Amylene, Cc.	Sulphuric Acid, Cc.	Upper Layer, Cc.	Polymers, % of Amylene Treated
1	80	120	60	75
2	260	390	195	75
3	500	750	384	76

The polymerization products were fractionated under diminished pressure and the bromine numbers [1] and the refractive indices were determined for all fractions. The data are tabulated in the following table.

TABLE 153

Amylene Polymers Formed in the Presence of Sulphuric Acid

Fraction No.	B.P., ° C.	Press., Mm. Hg	Amount, G.	n_D^{27}	Bromine, Number	Organic Analysis before Distillation	
						% C	% H
1	Below 55	10	8.5	1.4140	6		
2	55– 74	8	13	1.4229	25		
3	74– 79	7	10.5	1.4339	24		
4	80– 88.5	6	5.5	1.4445	27		
5	88.5– 96	6	7.5	1.4448	33		
6	96–107	6	12	1.4479	38	85.6	14.8
7	107–117	6	13.5	1.4511	38		14.7
8	117–130	6	21	1.4522	39		
9	130–152	6	29	1.4582	29		
10	152–169	6	19	1.4611	39		
11	169–175	6	7.5	1.4642	35		
12	Above 175		10	1.4642	35		

Distillation of the polymer formed in Expt. No. 3 gave the data shown in the following table. In column No. 6 of this table is indicated the number of minutes during which there was no change in the coloration of a 2% solution of potassium permanganate.[2]

From the above, the following conclusions may be drawn: The fraction boiling below 54–55° (10–17 mm.) and distilling at ordinary pressure at 140–145° contained *diamylene*, $C_{10}H_{20}$, and its amount did not exceed 5% of the total fraction, as indicated by

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[1] The bromine number was determined according to the method of Francis.

[2] The test with the 2% solution of potassium permanganate was made as follows: To 1.5 cc. of ethanol, one drop of the fraction to be tested and one drop of the potassium permanganate solution were added.

TABLE 154

Amylene Polymer Formed in the Presence of Sulphuric Acid
(*Expt. 3*)

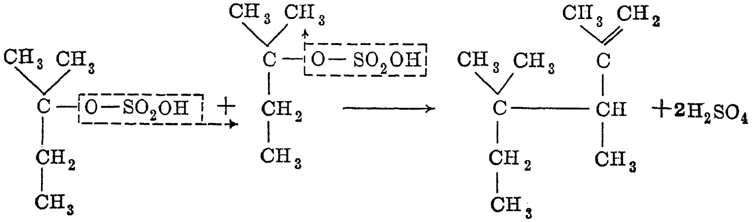
Fraction No.	B.P., ° C.	Press., Mm. Hg	Amount, G.	n_D^{23-24}	Minutes before Decoloration of 2% $KMnO_4$	Organic Analysis	
						% C	% H
1	Below 54	17	8	1.4177	3		
2	54– 56	7	16	1.4211	3	84.5	15.6
3	56– 65	7	5.5	1.428	3	84.1	15.6
4	65– 71	7	6	1.4337	3		
5	71– 79	7	9	1.4409	2.5	84.6	15.0
6	79– 86	7	14.5	1.4467	1.8	85.1	14.6
7	86– 97	7	11.0	1.4489	1.5	84.9	14.6
8	97–102	7	17.0	1.4510	1.5	84.9	14.7
9	102–108	7	19.0	1.4532	1.8	85.5	14.6
10	108–120	7	21.5	1.4555	1.8	85.2	14.7
11	120–126	7	18.0	1.4575	1.8	85.1	14.4
12	126–134	7	21.0	1.4588	1.8	84.9	14.5
13	134–143	7	13.0	1.4602		85.3	14.4
14	143–154	7	11.0	1.4619		85.4	14.9
15	154–162	7	11.0	1.4632		85.2	14.9
16	162–182	7	16.0	1.4651		85.5	14.2
17	Above 182	7	10				

the bromine number. The fraction was composed principally of saturated hydrocarbons. Likewise, fractions 2 and 3 contained considerable amounts of saturated hydrocarbons, chiefly $C_{10}H_{22}$, the carbon-hydrogen ratio for this formula (C, 84.5%; H, 15.5%) being close to the figures obtained. Fractions boiling at 154–162° at 6–7 mm. (at about 350° under ordinary pressure) consisted of hydrocarbons of the formula $C_{20}H_{40}$, 70% of which was tetra-amylene as inferred from the bromine number. The tests with potassium permanganate solution and nitrating mixture, the determination of the bromine numbers and the organic analyses showed that the low boiling fractions contained chiefly saturated hydrocarbons, while in the higher fractions of the polymerization products a considerable amount of olefins was present. Although the analyses showed that the higher fractions of the polymerization product contained a considerable amount of hydrocarbons having a double bond, no final decision can be given at present regarding their exact character. It is to be inferred from the constancy of the composition of the higher fractions that they consist chiefly of olefins, but whether or not naphthenes are also present is a moot question. In order to answer this question it would be necessary to hydrogenate these fractions and analyze the hydrogenated products.[1] In hydrogenating these fractions many difficulties would be encountered but such a study would furnish valuable information concerning the character of the polymerization products of olefins.

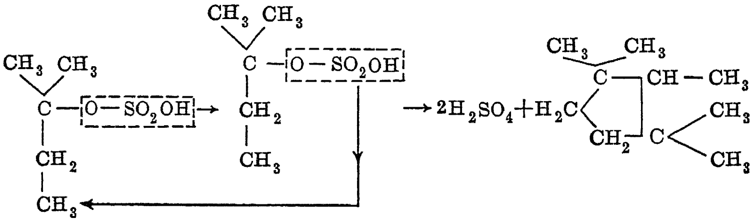
The hypothesis which we proposed for the explanation of the catalytic reactions of polymerization and dehydration by catalysts containing the hydroxyl group (refer to chapter on Theoretical Principles of Catalytic Processes) gives an insight as to the mode of formation of saturated hydrocarbons by the polymerization of amylene. The formation of the diamyl ester of sulphuric acid and its decomposition into a saturated hydrocarbon may be expressed as follows:

$$C_5H_{11}—O—SO_2—O—C \qquad C_{10}H_{22} + SO_3 + O$$

From two molecules of the mono-amyl ester of sulphuric acid a polymer of olefinic character can be formed, according to the following scheme:



The formation of a naphthene is also possible according to the following equation:



It is supposed that an equilibrium exists between the mono- and di-esters of sulphuric acid and that the character of the equilibrium depends principally upon the structure of the olefins and the concentration of the sulphuric acid.[1] Experiments made with various olefins under pressure for the purpose of obtaining the diesters confirmed this assumption.

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[1] This question can also be settled by means of destructive hydrogenation (in publication).

Action of Sulphuric Acid upon Ethylene under Pressure

The absorption of ethylene by sulphuric acid was studied by Berthelot [2] and Butlerow.[3] It proceeds slowly at 70–80°, and the reaction product is the mono-ethyl ester of sulphuric acid.

We made experiments [4] on the absorption of ethylene by sulphuric acid under pressure in a silver lined Ipatieff rotating bomb equipped with a glass tube of 400 cc. capacity. The sulphuric acid was introduced into the glass tube, ethylene was pumped in, and the reaction was considered finished when the pressure stopped falling. In a typical experiment 90 cc. of 92% sulphuric acid at room temperature under 65 atmospheres initial pressure of ethylene yielded 140 cc. of liquid product in 6 hours. The amount of ethylene absorbed corresponded very closely to the formation of diethyl sulphate. The reaction product in the glass tube was poured into ice water and the heavy oil which separated was washed with water, neutralized with barium carbonate, filtered, dried; 99 cc. was distilled at 6 mm.: (1) up to 70°, 0.5 g.; (2) 70–71°, 52 g.; (3) 71–72°, 27 g.; (4) above 72°, 9 g.; n_D^{20}, 1.4059; d_{20}, 1.1731; sulphur content, 21.3%. The theoretical value for $(C_2H_5)_2SO_4$ is 20.3%. According to its properties and analysis the product was diethylsulphate. The freshly distilled product was a colorless oil, which acquired a violet coloration on exposure to air. The yield was good and no polymers were present in the reaction product.

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[1] Recent investigations on the action of catalysts, H_3PO_4, $AlCl_3$, etc., on various hydrocarbons have shown that olefins can isomerize into naphthenes, and the latter, at the moment of their formation, can liberate atoms of hydrogen, thus forming unsaturated mono- and polycyclic hydrocarbons. The liberated atomic hydrogen is able to hydrogenate the olefins, forming paraffins. If such a reaction takes place in the presence of phosphoric acid, one can expect that a similar reaction will take place, to a certain extent, in the presence of sulphuric acid. Assuming such a hypothesis we can easily explain what happens to the oxygen which is formed on decomposition of the dialkyl ester of sulphuric acid, the other products of the decomposition being paraffins and sulphur trioxide. The liberated hydrogen combines with the oxygen and as a result sulphuric acid is regenerated.

Similarly, one can suppose that a cyclization of olefins having a high molecular weight occurs at the time of decomposition of the mono-ester of sulphuric acid molecule.

[2] Berthelot, Ann. chim. phys., (3), *43*, 485 (1855).

[3] Butlerow, Ber., *6*, 196 (1873).

[4] Ipatieff and Pines, unpublished results.

Action of Sulphuric Acid upon Propylene

According to the investigations of Preston,[1] the passage of propylene through sulphuric acid (97%) at 25° C. results chiefly in the formation of monopropyl sulphate together with a small amount of dipropyl sulphate and a light oil consisting of saturated hydrocarbons. Experiments on the absorption of propylene by sulphuric acid (96%) were repeated at 0° and at room temperature. They showed that up to 76% of the propylene was absorbed by sulphuric acid (96%). Monopropyl sulphate, soluble in water, was the chief product; and only an insignificant amount of oil was obtained. When the reaction of sulphuric acid with propylene is made under pressure the results are altogether different as the following experiment shows.

Propylene was pumped into a bomb containing sulphuric acid until it was no longer absorbed. The reaction product did not contain any light oil and when poured into ice water, a heavy oil separated which was washed with water and dried. It consisted chiefly of diisopropyl sulphate with an admixture of some monoisopropyl sulphate. Thus, there is no doubt of the formation of the di-esters of sulphuric acid by the action of olefins and the decomposition of these esters may be a step in the formation of saturated hydrocarbons. This is a possible explanation of the formation of saturated hydrocarbons in the polymerization of olefins with sulphuric acid.

POLYMERIZATION OF OLEFINS BY PHOSPHORIC ACID

It is a known fact that the polymerization of olefins under the influence of sulphuric acid at low temperatures proceeds with ease, particularly with hydrocarbons containing the groupings $—C{=}CH_2$ and $—C{=}CHR$. It seemed interesting to study the polymerization of olefins by means of other catalysts. It should be noted that the temperature used in polymerization by sulphuric acid cannot be raised because of side reactions which completely alter the course of the reaction and promote the formation of high molecular weight polymers. Because of these considerations, the study of the polymerization of olefins under the influence of phosphoric acid was undertaken, and particularly the absorption of the simplest olefins by phosphoric acid under pressure.

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[1] Preston, J. Soc. Chem. Ind., *40*, 145 (1921).

Formation of the Ethyl Ester of Phosphoric Acid

The action of phosphoric acid upon ethylene at ordinary pressure was first studied by Müller.[1] Absorption of ethylene by orthophosphoric and pyrophosphoric acids at 115–145° C. proceeded very slowly, 1200 cc. of ethylene being absorbed in 17 days. The reaction product (1.8 g.) consisted of the mono-ethyl ester of phosphoric acid; no liquid hydrocarbons were found.

We investigated the absorption of ethylene by phosphoric acid, working under pressure in the apparatus described above and using 95% orthophosphoric acid. In certain cases, promoters such as copper, cuprous chloride, and others were added. The reaction started at a temperature of about 190–200° and its course could be followed by observing the change in pressure. As can be seen from the following table the pressure dropped quite rapidly.

TABLE 155

CHANGE IN PRESSURE DURING THE POLYMERIZATION OF PROPYLENE BY ORTHOPHOSPHORIC ACID

TIME, HRS.	PRESS., ATMS.	T., ° C.
0	103	193
2	91	196
4	79	202
6	73	204
8.5	68	204
10.3	62	204
12.3	62	204

When the pressure ceased falling, the experiment was considered completed. At the end of the reaction the residual gas consisted of pure ethylene. The reaction product was poured into ice water whereupon the entire product dissolved. When the solution was shaken with ether, there was only one case which resulted in the extraction of any oil, and then only about 1 cc.

The aqueous solution consisted of phosphoric acid and the ethyl ester of phosphoric acid (the solution was diluted with water in the ratio of 1 volume of phosphoric acid to 12 volumes of water). Barium carbonate and barium hydroxide were added to the solution at 60° until it was slightly alkaline to phenolphthalein. Barium phosphate precipitated out under these conditions, but the barium salt of the ethyl ester of phosphoric acid remained in solution. The solution was filtered and alcohol was added in order to precipitate the barium salt of ethyl phosphoric acid. The barium salt precipitated from the solution in well-defined needle-like crystals which were readily soluble in water but insoluble in alcohol. Analysis showed that this substance was the barium salt of the mono-ethyl ester of phosphoric acid:

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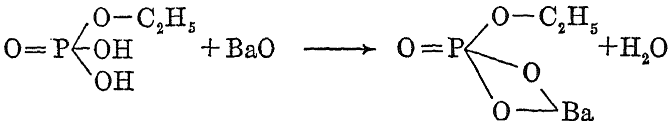
[1] Müller, Ber., *58*, 2105 (1925).



Experiments under similar conditions were carried out with propylene, which indicated that the isopropyl ester of phosphoric acid was formed. These esters are not stable and decompose at a higher temperature with the formation of polymers. These experiments made it possible to explain the mechanism of the polymerization reaction with phosphoric as well as with other acids. (See chapter on "Theoretical Principles for Catalytic Reactions.")

Polymerization of Amylene by Phosphoric Acid

The first experiments on polymerization of olefins were carried out with amylene,[1] b.p., 36–38°. Up to the time of our investigations the literature contained no information on this reaction. It is well known that the above amylene consists of two isomers, trimethylethylene and methylethylethylene, the former comprising about 70% of the total. Amylene was subjected to polymerization at atmospheric pressure and also at superatmospheric pressure.

For the polymerization of amylene under pressure, use was made of the bomb previously described which had a silver lining and which contained a glass liner, the latter being provided with a ground glass stopper with a capillary opening. Phosphoric acid and amylene were poured into the glass tube, the bomb was closed, and nitrogen pressure was applied. The apparatus was set in rotation at 200° and the reaction was allowed to continue for a certain length of time. The reaction product consisted of two layers, an upper layer of polymerization products of amylene, and a lower layer of unchanged phosphoric acid.

The upper layer, after washing and drying, was distilled and analyzed. The data are summarized in the following table:

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[1] Ipatieff and Pines, unpublished results (1931).

TABLE 156

POLYMERIZATION OF AMYLENE IN THE PRESENCE OF PHOSPHORIC ACID

Expt. No.	Phosphoric Acid, G.	Amylene, G.	T., ° C.	Time, Hrs.	Upper Layer	
					G.	% of Amylene Charged
1	119	70	210	11	45	64.3 [a]
2	83	75	210	12	65	86.6 [a]
3	83	75	200	12	59	78.6 [a]
4	80	78	100	7.5	70	90
5	58	50	60	8.0	48	90
6	11	60	58	7.5	58	96.6
7	10	60	100	7.5	57	95.0

[a] Due to the fact that a large amount of phosphoric acid was used an emulsion formed and the yield of the upper layer was small.

The products from the first three experiments were combined, distilled, and analyzed.

TABLE 157

AMYLENE POLYMERS FORMED IN THE PRESENCE OF PHOSPHORIC ACID

Fraction No.	B.P., ° C.	Pressure	Product					
			G.	n_D^{20}	d^{20}	Bromine No.	Analysis	
							% C	% H
1	43– 54	atmos.	4.5	1.3740		46		
2	54– 67	atmos.	6.5	1.3752		39	83.2	16.1
3	67– 69	atmos.	8.5	1.3775	0.6456	39		
4	69– 82	atmos.	6.0	1.3853	0.6655	27	83.3	16.0
5 [a]	82–149	atmos.	8.0					
6	149–171	atmos.	26.0					
7	171–174	atmos.	16.0					
8	66– 77	7 mm. Hg	11.0	1.4490	0.7836	88	88.7	14.2
9	77– 80	7 mm. Hg	15.5	1.4549	0.7983	85		
10	80– 84	7 mm. Hg	9.5	1.4612	0.8124	84	86.3	13.7
11	84–104	7 mm. Hg	16.5	1.4692	0.8291	77	86.4	13.6
12	104–121	7 mm. Hg	12.0	1.4863	0.8632	59	87.1	12.9
13	121–138	7 mm. Hg	5.0	1.5047		57		

[a] Fractions 5, 6, and 7 (distilling between 82° and 174°) were combined, redistilled, and examined.

On the basis of the data obtained, the following conclusions may be drawn:

(1) Phosphoric acid is a true catalyst for the polymerization of amylene.

(2) The best temperature for the polymerization of amylene is between 60° and 100°.

TABLE 158

AMYLENE POLYMERS

Fraction No.	B.P., ° C. @ 760 Mm. Hg	Product					
		G.	n_D^{20}	d^{20}	Bromine No.	Analysis	
						% C	% H
a	55–109	3	1.3970		25	83.5	15.9
b	109–139	6	1.4193	0.7159	54	84.4	15.0
c	139–149	6.5	1.4252	0.7354	75		
d	149–155	7.5	1.4313	0.7435	80	85.0	14.6
e	155–166	8.0	1.4360	0.7548	93		
f	166–174	4.0	1.4408	0.7661	87	85.4	14.3
g	174–194	8.0	1.4472	0.7800	89		
h	> 194	5.0	1.4638	0.8141	66		

(3) The distillation curve of the product rises rapidly to 145° since diamylene is the principal product (about 72%) even at low temperatures.

(4) The side reaction products are: saturated hydrocarbons (present in the lower boiling fractions) and more unsaturated hydrocarbons, in all probability corresponding to C_nH_{2n-2} and C_nH_{2n-6} aromatic hydrocarbons (present in the higher boiling fractions).

(5) The low bromine number, the organic analysis, and the result of treatment with sulphuric acid serve as proof of the presence of saturated hydrocarbons in the low boiling fractions. The hydrocarbons in the lower fractions, insoluble in sulphuric acid, are paraffinic and are not acted upon by either nitrating mixture or potassium permanganate solution.

(6) The products obtained by the polymerization of amylene with sulphuric acid and with phosphoric acid differ greatly. For example, the corresponding fractions from these two methods of polymerization of amylene have the different properties shown below:

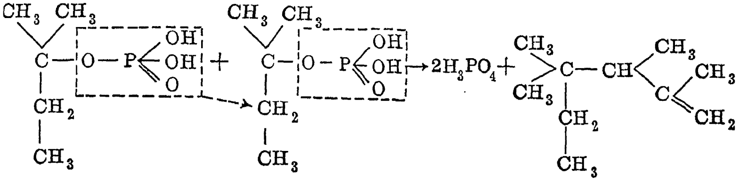
TABLE 159

COMPARISON OF PROPERTIES OF AMYLENE POLYMERS FORMED IN THE PRESENCE OF ACID CATALYSTS

B.P., ° C.	Press., Mm. of Hg	Catalyst	n_D^{20}	d^{20}	Organic Analysis	
					% C	% H
175–186	7	H_2SO_4	1.4467	0.7892	85.4	14.6
176–184	7	H_3PO_4	1.4612	0.8124	86.1	13.7

(7) It was observed that the hydrogen content of the higher fractions is less when using phosphoric acid as catalyst. The hydrogen thus liberated hydrogenates the lighter olefins, forming saturated hydrocarbons.

(8) The polymerization of amylene under the influence of phosphoric acid passes through the formation of the unstable amylester of phosphoric acid and proceeds by virtue of the withdrawal of the elements of phosphoric acid from two molecules of ester according to the same type of scheme proposed for the reaction of amylene with sulphuric acid.



From the two isomers present in commercial amylene, five isomeric diamylenes ($C_{10}H_{20}$) may be obtained by the removal of hydrogen atoms from different carbons. The hydrogenation of diamylenes under pressure in the presence of nickel oxide yielded only three isomeric decanes, $C_{10}H_{22}$; the product of hydrogenation boiled at 153–166°. Their analysis gave the following data:

Fraction boiling at 153–158°: d_{24}, 0.7479; C, 84.1%; H, 15.7%.
Fraction boiling at 158–166°: d_{24}, 0.7532; C, 84.1%; H, 15.5%.
Calculated for $C_{10}H_{22}$: C, 84.5%; H, 15.5%.

The paraffinic hydrocarbon $C_{10}H_{22}$ obtained did not react with nitrating mixture or with potassium permanganate solution. The nature of the more unsaturated hydrocarbons present in the higher fractions has not yet been determined. However, it may be inferred that the higher boiling fraction consists of aromatic hydrocarbons and of hydrocarbons of a cyclic nature with double bonds.

Polymerization of Amylene by Phosphorous Acid

Phosphorous acid had never been previously used as catalyst for polymerization. In order to confirm the hypothesis explaining catalytic polymerization, dehydration, etc., the action of this acid upon amylene was studied. The reaction was performed in the type of autoclave previously described. Thirty grams of phosphorous acid and 42 g. of amylene (b.p., 34–37°) were placed in the glass liner of the autoclave which was rotated and heated at 177–190° for six hours. The reaction product consisted of two layers, the lower layer containing unchanged phosphorous acid, and the upper layer, the product of the polymerization of amylene. The latter was washed, dried, and distilled. Four experiments were made and 148 g. of material was distilled.

TABLE 160

AMYLENE POLYMERS FORMED IN THE PRESENCE OF PHOSPHOROUS ACID

FRACTION NO.	B.P., ° C.	AMOUNT, G.	n_D^{29}
1	33– 50	59	
2	50–138	5	
3	138–147	19	1.4289
4	147–158	31	1.4336
5	158–160	15	1.4362
6	160–227	10	1.4474

The first fraction consisted chiefly of unchanged amylene. The fractions distilling at 138–160°, according to their organic analyses and properties, were mixtures of isomeric diamylenes. In the last fraction, triamylene was present. It is evident from the distillation data that phosphorous acid is also a true polymerization catalyst.[1]

Polymerization of Amylene by Organic Acids [2]

When studying the polymerization of olefins by sulphuric and phosphoric acids, it was assumed that the formation of unstable intermediate compounds takes place. These unstable esters decompose and the polymers result from the combination of the olefins liberated *in statu nascendi*. Since the literature refers to investigations [3] on the equilibrium between acid, olefin, and ester, it seemed interesting, as a test of this polymerization hypothesis, to check the possibility of the formation of polymers by the action of organic acids upon olefins.

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[1] Ipatieff and Kurbatov polymerized isobutylene in the presence of perchloric acid. Depending upon the conditions, there was obtained either esters of perchloric acid or polymers of isobutylene.

[2] Ipatieff and Pines, unpublished results.

[3] Konowalov, Z. physik. Chem., *1*, 63 (1887); *2*, 380 (1888). Menschutkin, Ann. chim. phys., (5), *20*, 229 (1880).

Trichloracetic acid and tartaric acid were used for the investigation. The reaction was performed in the same apparatus as previously used. By the action of trichloracetic acid (15 g.; initial pressure of ethylene, 61 atmospheres; 190° C. for 8 hours) a product was obtained which boiled at 160°, was heavier than water, and had n_D^{18}, 1.4512. This product, according to its properties and analysis, was ethyltrichloracetate, $CCl_3—COOC_2H_5$. By the action of trichloracetic acid (13 g.) upon amylene (151 g.) at 190° C. for 8 hours with an initial nitrogen pressure of 43 atmospheres, a liquid product resulted which boiled at 150–165°; C, 85.5%; H, 14.5%. Its properties and analysis showed that it was *diamylene*, $C_{10}H_{20}$.

By the action of 15 g. of dry tartaric acid upon 50 g. of amylene at 200° for 6 hours under an initial nitrogen pressure of 45 atmospheres, a liquid product was obtained, 42 g. of which was distilled and examined.

TABLE 161

Amylene Polymers Formed in the Presence of Tartaric Acid

Fraction No.	B.P., ° C.	Amount, G.	n_D^{20}	Analysis	
				% C	% H
1	30–115	18			
2	115–146	6	1.4282	85.2	14.6
3	146–163	15	1.4401	85.9	14.5

All these data indicate that the third fraction consisted of diamylene and that tartaric acid is a polymerization catalyst. Acetic acid at temperatures below 200° is unable to polymerize amylene under an initial nitrogen pressure of 43 atmospheres, but perhaps the reaction might take place at higher temperatures.

It is to be inferred that organic acids are able to polymerize olefins and that this reaction also proceeds with the intermediate formation of esters similar to those formed with sulphuric and phosphoric acids.

Polymerization of Ethylene in the Presence of Phosphoric Acid

The polymerization of ethylene in the presence of phosphoric acid has not been investigated previously. Montmollin [1] reported that liquid hydrocarbons were formed by reacting ethanol with phosphoric acid at atmospheric pressure and at a temperature of 210–240°. In this case, the ethanol was dehydrated to yield ethylene which subsequently underwent polymerization. Montmollin reported the existence of paraffin, olefin, naphthene, and aromatic hydrocarbons in the resulting liquid product. He did not determine the composition of the gas formed by the reaction.

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[1] Montmollin, Bull. soc. chim., *19*, 242 (1916).

Ipatieff and Pines [1] found that the "polymerization" of ethylene at 330° under pressure in the presence of phosphoric acid yielded a hydrocarbon mixture consisting approximately of 46% paraffins, 7% unsaturated hydrocarbons,[2] 21% naphthenes, and 26% aromatics. These results on the composition of the ethylene "polymer" were obtained by separating it into fractions of different boiling ranges and determining the hydrocarbons present in each fraction.

The apparatus consisted of an electrically heated, three-liter Ipatieff rotating autoclave provided with pressure gage, valve, thermocouple well, and a Pyrex liner to prevent corrosion of the steel walls. The autoclave was charged with 200 g. of 90% phosphoric acid and ethylene was added to 50 kg./cm.^{2} pressure. The bomb was heated at 330° for 5–6 hours after which it was cooled and more ethylene was introduced. This procedure was repeated several times until the desired amount of liquid product had been obtained. The following table shows the initial pressure of the ethylene introduced and the pressure registered during the reaction. After 5 to 6 hours of heating the pressure remained practically constant.

TABLE 162

"POLYMERIZATION" OF ETHYLENE

REFILLING No.	ETHYLENE CHARGED @ 25° TO Kg./Cm.^{2}	PRESS., KG./CM.^{2}		REFILLING No.	ETHYLENE CHARGED @ 25° TO Kg./Cm.^{2}	PRESS., KG./CM.^{2}	
		Max. @ 330°	Final @ 25°			Max. @ 330°	Final @ 25°
1	40	92	24	4	50	132	15
2	50	130	14	5	50	150	12
3	50	138	15	6	50	157	12

At the end of the experiment after the bomb was cooled to room temperature, the gas was passed through two traps in series maintained at −78° by a mixture of solid carbon dioxide and acetone, and the uncondensable gas was collected in a gasholder over brine. It was necessary to heat the bomb to 40° in order to remove dissolved gas from the liquid product.

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[1] Ipatieff and Pines, Ind. Eng. Chem., *27*, 1364 (1935).

[2] They consist of olefinic, cycloölefinic, and aromatic hydrocarbons with unsaturated side chains.

A portion of the condensable gas was distilled through a low temperature Podbielniak column.[1] Another portion was analyzed by the usual gas analysis method. Combination of the two methods permits accurate determination of the gas composition. It was found that the condensable gas consisted of 98% of isobutane (18.8% by weight of the ethylene which underwent change) [2] and 2% of n-butene. Sixteen liters of gas incondensable at −78° was collected. Besides unreacted ethylene it contained 21.2% of hydrogen. Calculated on a volume basis it represents 0.6% of the total ethylene which reacted.

The liquid product was separated from the phosphoric acid, washed with 15% sodium hydroxide solution and then by distilled water, after which it was dried over calcium chloride and fractionally distilled. Index of refraction and bromine number were determined on most of the fractions. The results obtained are summarized in Tables 163–165.

The fraction of the liquid product boiling up to 90° was almost entirely paraffinic, its olefin content being negligible. The cut boiling from 140 to 155° contained 10% of paraffins, 25% of olefins, and 65% of naphthenes. The percentage of naphthenes decreased in the higher boiling fractions until it became zero in the fraction boiling between 285 and 300°. Paraffin hydrocarbons were not found in the fraction boiling from 225 to 241°. The aromatic content of the fractions increased regularly with rise in boiling point. The fraction boiling between 285 and 300° contained 85% of aromatic hydrocarbons. From the carbon-hydrogen analysis it can be concluded that the aromatic hydrocarbons were composed of a mixture of alkylbenzenes and of cyclohexylphenyl derivatives. In the case of naphthenes, the higher boiling fractions apparently contained polycyclic members of this group. Aromatic hydrocarbons with unsaturated side chains are probably present in the fractions boiling at 241° and higher.

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[1] Podbielniak, Ind. Eng. Chem., Anal. Ed., *5*, 172 (1933).

[2] An experiment was made at the same temperature and with the same initial pressure of ethylene, but the time of heating was eight hours. The bomb was not refilled with fresh ethylene. The resulting product contained 14% of isobutane. This shows that the time of heating has no decided effect upon the amount and character of the gases produced.

TABLE 163

Distillation of Ethylene "Polymer" and Properties of the Fractions

Fraction No.	B.P., ° C.	Weight, G.	%	Total % Over	Bromine No.	n_D^{20}
1	-12[a]	118.0	18.8			
2	13-24.5[b]	6.9	1.1	19.9		
3	24.5-30.0	12.2	1.8	21.7	3	
4	30.0-30.5	6.9	1.1	22.8		
5	30.5-32.5	6.6	1.1	23.9		
6	33.5-37.4	6.3	1.1	25.0		
7	37.4-59.0	12.8	2.0	27.0		
8	59.0-60.5	39.0	6.0	33.0	2	
9	60.5-70.0	36.2	5.5	38.5	6	1.3785
10	70.0-84.0	16.5	2.5	41.0	8	1.3822
11	84- 95	14.0	2.2	43.2	9	1.3911
12	95-110	16.0	2.5	45.7	14	1.4025
13	110-125	12.5	2.0	47.7	16	1.4111
14	125-140	11.0	1.7	49.4	23	1.4222
15	140-155	16.0	2.5	51.9	33	1.4325
16	155-170	12.0	1.9	53.8	37	1.4415
17	170-185	13.0	2.0	55.8		1.4520
18	185-205	15.0	2.3	58.1		1.4678
19	205-225	11.5	1.8	59.9	32	1.4852
20	225-241	29.0	4.0	63.9	20	1.4978
21	241-250	32.0	5.0	68.9	13	1.5061
22	250-263	28.5	4.4	73.3	8	1.5120
23	263-276	27.0	4.2	77.5	7	1.5170
24	276-285	33.0	5.2	82.7	6	1.5220
25	285-300	41.5	6.4	89.1	6	1.5225
26	160-174 8 mm.	14.0	2.1	91.2		1.5309
27	174-185 8 mm.	12.0	1.7	92.9		1.5378
28	185-200 8 mm.	14.0	2.2	95.1		1.5483
29	200-210 8 mm.	10.0	1.5	96.6		1.5616
30	Residue	20.0	3.0	99.6		

[a] This fraction corresponds to isobutane.

[b] The fractions boiling up to 60° were tested with a 2% solution of potassium permanganate. No unsaturates were found.

In order to explain the presence of the different types of hydrocarbons in the product obtained from the "polymerization" of ethylene, the following mechanism was suggested.

(1) The first step in this reaction is the formation of ethyl phosphates.

TABLE 164

Analysis of Products Formed by the 'Polymerization" of Ethylene at 330°

B.P., ° C.	−12 [a]	59–60.5 [b]	140–155	175–225	175–225	241–250	241–250	285–300	185–200° C. 8 Mm.
ANALYSIS BEFORE TREATMENT WITH SULPHURIC ACID									
C%		83.6		87.1	87.1	88.4	88.4	88.3	88.4
H%		16.35		12.9	12.9	11.6	11.6	11.6	11.5
Br_2 No.		2	33	30	30	13	13	6	
Mol. Wt.		89	131	165	165	182	182	224	293
		0.654	0.778	0.830	0.830	0.890	0.890	0.920	
			1.4325	1.4655	1.4655	1.5061	1.5061	1.5255	
ANALYSIS AFTER TREATMENT WITH SULPHURIC ACID									
H_2SO_4			96	96	15% Fuming	96% H_2SO_4	15% Fuming	96% H_2SO_4 [e]	
C%			85.6	86.5	85.8	88.2	86.8	88.4	
H%			14.6	13.4	14.3	11.8	13.3 [d]	11.7 [f]	
n_D^{20}			1.4315	1.4570	1.4751	1.5062	1.4751		
COMPOSITION OF FRACTIONS, %									
Unsaturates	0	0	25	24		10		15	
Paraffins	100	100	10	0		0		0	
Naphthenes	0	0	65 [c]	61		14		0	
Aromatics	0	0	0	15		76		85	

[a] Consists of isobutane.

[b] Corresponds to hexane.

[c] The naphthenes were converted into aromatics by dehydrogenation over palladinized asbestos.

[d] Dicyclic hydroaromatics are probably present.

[e] The product was completely soluble in fuming sulphuric acid (15% SO_3).

[f] From the carbon-hydrogen analysis before and after the treatment with sulphuric acid it can be assumed that aromatic hydrocarbons with unsaturated side chains are present.

TABLE 165

Properties of Products Formed by Hydrogenation of Different Fractions of Ethylene "Polymer"

Fraction Hydrogenated, B.P., ° C.	Temperature of Hydrogenation, ° C.	Hydrogenated Product			
		% C	% H	n_D^{20}	d_4^{20}
175–225	240	85.8	14.2	1.4400	
241–250	220	87.2	12.5	1.4840	
241–250	330	85.8	14.1	1.4568	0.831
285–300	220	88.0	11.9	1.5140	0.910
285–300	350	86.1	13.9 [a]		0.858

[a] The carbon-hydrogen analysis shows the presence of polycyclic naphthenes.

(2) Ethyl phosphates being unstable at higher temperatures decompose to give ethylene polymers and naphthenes.

(3) Naphthenic hydrocarbons dehydrogenate to form aromatic hydrocarbons.

(4) Olefin hydrocarbons are hydrogenated to paraffins by the hydrogen resulting from the dehydrogenation of the naphthenes to aromatics.

The last two reactions take place simultaneously; the hydrogen, being *in status nascendi* reacts with the olefins (molecular hydrogen under the same conditions does not react with olefins).[1] The formation of paraffin and aromatic hydrocarbons is due to *intermolecular hydrogenation-dehydrogenation reactions.*

Besides the four main reactions mentioned as taking place in the "polymerization" of ethylene, the following may also occur:

(a) Alkylation of aromatic hydrocarbons with ethylene to form ethylbenzenes.[2]

(b) Partial dehydrogenation of naphthenes to yield polycyclic naphthenes.

(c) Isomerization of olefinic hydrocarbons. (This reaction will be discussed fully in connection with the mechanism of the formation of isobutane.)

The fact that the heating of ethylene under pressure in the presence of phosphoric acid yielded a mixture of different types of hydrocarbons makes it seem inappropriate to call this reaction one of polymerization. We propose to call this "conjunct polymerization." Polymerization is understood as a reaction in which two or more like molecules combine to form compounds retaining the same functional group as the original substance but having molecular weights which are multiples of that of the original compound.

The *formation of isobutane* was unexpected in the "polymerization" of ethylene. The isobutane formed was equal to 18.8% by weight of the ethylene which underwent change. From the above mechanism of the reaction it would be expected that the dimer of ethylene would be 1- or 2-butene, which could be hydrogenated to n-butane. The formation of isobutane could be explained by the isomerization of 1- or 2-butene into isobutene [3] with subsequent reduction of isobutene into isobutane.[4]

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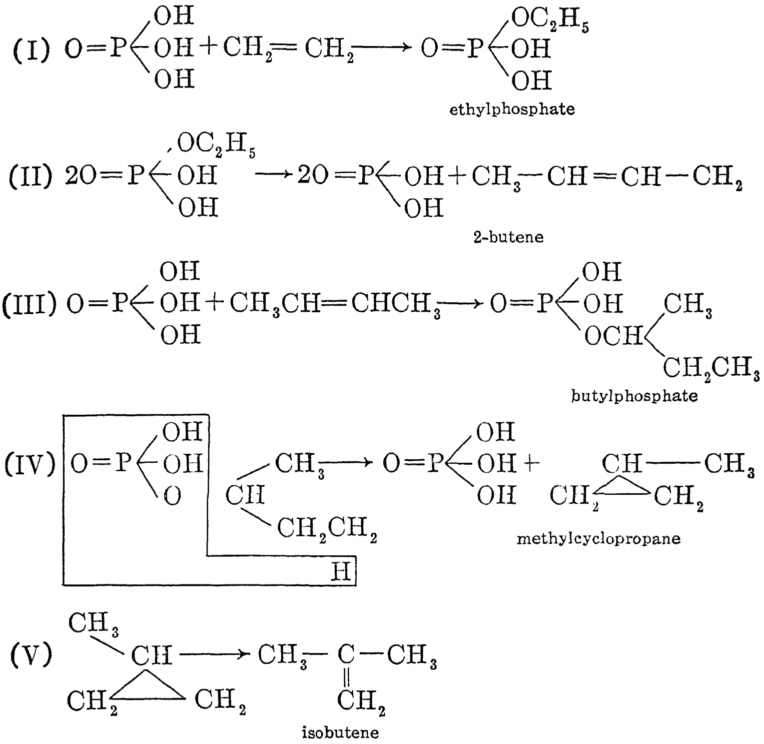
[1] Ipatieff and Pines, unpublished results.

[2] Ipatieff and Pines succeeded in preparing ethylbenzene by reacting ethylene and benzene in the presence of phosphoric acid.

[3] Ipatieff, Ber., *36*, 2002 (1905); *36*, 2014 (1905); *40*, 1827 (1909).

[4] Ipatieff and Pines, unpublished work. 1-Butene was heated at 330° with

The schematic representation of the reaction is as follows:



During the reaction methylcyclopropane is probably formed, but being unstable decomposes into isobutene, which in turn is hydrogenated by the hydrogen liberated from the dehydrogenation of naphthenes.

The following methods were used to prove the presence of the different types of hydrocarbons.

(1) The olefin content was determined with 96% sulphuric acid at 0° by treating one volume of the product from the different fractions with two volumes of the acid. The mixture was shaken cautiously for 15 to 20 minutes, after which it was allowed to stand for 15 minutes, and then the olefin-free layer was separated,

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phosphoric acid and hydrogen at an initial pressure of 100 atms. Liquid polymers were formed. The gaseous hydrocarbons were collected and analyzed by means of Podbielniak distillation and Göckel gas analysis. Of the gas condensable at −78°, 50% was isobutane; small amounts of n-butane formed and the remainder was unreacted butene. The isobutane formed was equivalent to 6% of the butene reacting.

washed, dried, and distilled. It was important to separate the hydrocarbon layer from the sulphuric acid at once, since with longer standing higher polymeric compounds would be liberated from the sulphuric acid layer and pass into the olefin-free layer.

(2) The degree of unsaturation was shown by the bromine number.

(3) The aromatic hydrocarbon content of the different fractions was determined by treating them with fuming sulphuric acid (15% SO_3). One volume of the product was treated with two volumes of fuming sulphuric acid (15% SO_3) at 0°. Sometimes this treatment had to be repeated in order to remove the last trace of aromatics.

The products after treatment with 96% and also with fuming sulphuric acid boiled within the same range as the original fractions.

(4) The different fractions were hydrogenated at 220–240° in the presence of nickel oxide under an initial hydrogen pressure of 100 atms. using cyclohexane as a solvent. At this temperature only the olefinic hydrocarbons were hydrogenated.

(5) Hydrogenation was made also at 330–360° in order to convert the aromatic into hydroaromatic hydrocarbons.

(6) Carbon and hydrogen analysis was made on each fraction before and after the above-mentioned treatments. The naphthenes were also identified by passing them over heated palladinized asbestos, by which treatment the naphthenes were dehydrogenated to aromatic hydrocarbons.

The bromine number and the treatment with 96% sulphuric acid furnished data as to the olefinic content of each fraction. In view of the fact that no aromatic hydrocarbons were present in the fractions boiling up to 200°, the treatment with sulphuric acid gave a reliable indication as to the amount of olefinic hydrocarbons present. The higher boiling fractions contained both olefinic and aromatic hydrocarbons, but under our experimental conditions (at 0°) the high boiling aromatic hydrocarbons are not alkylated with the high boiling olefinic hydrocarbons in the presence of 96% sulphuric acid. Here, therefore, sulphuric acid treatment could be used safely as a method of separating olefinic hydrocarbons from the other types of hydrocarbons.

The chemical composition of the different fractions was estimated by comparing the carbon-hydrogen analyses before and after the treatment of the fractions with 96% sulphuric acid and with fuming sulphuric acid (15% SO_3). This means that the carbon-hydrogen analyses were made on the original product, on the olefin-free product, and also on the material remaining after the removal of both olefins and aromatics. The carbon-hydrogen analyses were compared also with the analyses of the product obtained after all the olefins were converted into paraffins by hydrogenation at 220–240°, and of the product obtained after the aromatic hydrocarbons were converted into hydroaromatic by hydrogenation at 360°. The method of calculation will be shown on a few examples.

Fraction 140–155°.—After treatment with 96% sulphuric acid the product was stable toward nitrating mixture which indicates the absence of aromatic hydrocarbons. The hydrogen content of the olefin-free fraction was 14.55%. The empirical formula for the paraffins in this fraction is $C_{10}H_{22}$ which corresponds to a hydrogen content of 15.5%. The hydrogen content of naphthenes is 14.37. Therefore, the olefin-free fraction consisted principally of naphthenic hydrocarbons. It was calculated that (based on the original product) this fraction consisted of 65% of naphthenes and 10% of paraffins. The proportions of the different types of hydrocarbons like paraffins, naphthenes, and aromatics are not claimed to be absolute since they are based on carbon-hydrogen analysis.

Also the presence of naphthenes in this particular fraction was proven by dehydrogenation over palladinized asbestos [1] to aromatic hydrocarbons.

Fraction 241–250°.—From Table 164 it is seen that this fraction consisted of:

10%	Olefins with	empirical	formula	$C_{14}H_{28}$	(H_2	content	14.37%)
14%	Dicyclic naphthenes	"	"	$C_{14}H_{26}$	("	"	13.4%)
76%	Aromatics	"	"	$C_{14}H_{22}$	("	"	11.66%)

This fraction was hydrogenated at 220°, so that only the olefins were reduced to give paraffin hydrocarbons with an empirical formula of $C_{14}H_{30}$ and a hydrogen content of 15.25%. Therefore, the hydrogen content of the product after hydrogenation should have been:

$$(0.10 \times 15.25\%)(0.14 \times 13.4\%)(0.76 \times 11.66\%) = 12.25\%$$

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[1] Zelinsky and Borissov, Ber., *57*, 1005 (1924).

The hydrogen content of the product after this hydrogenation was found to be 12.51%.

One part of the original fraction was hydrogenated at 330° by which the olefins were converted into paraffins and the aromatics into hydroaromatic hydrocarbons with the empirical formula of $C_{14}H_{28}$; on this basis it was calculated that the hydrogen content of the hydrogenated product should be 14.26%, as compared with the experimental results; C, 85.82%; H, 14.14%.

The total amount of aromatics formed was calculated as follows:

TABLE 166

B.P., °C.	% by Weight of the Total Polymers Formed	% by Weight of Aromatics in Each Fraction	% by Weight of Aromatics Based on the Total Polymers Formed
Below 175		0	0
175–225	4.0	15	0.6
225–241	4.0	35 [a]	1.4
241–250	5.0	76	3.8
250–285	13.8	76 [a]	10.5
285–300	6.4	85	5.4
160–210° C., 8 mm.	5.4	85	4.6
Total of aromatics present			26.3% [b]

[a] The percentage of aromatics was based on data not reported in this paper.

[b] Actually the amount of aromatics present was higher since the aromatics with an olefinic side chain were reported as unsaturates.

Conclusions

(1) Ethylene, under an initial pressure of 50 kg./cm.^{2} at 25°, was heated at 330° in the presence of phosphoric acid. A hydrocarbon mixture resulted which contained approximately 46% of paraffins, 7% of unsaturated hydrocarbons, 21% of naphthenes, and 26% of aromatics.

(2) The formation of paraffin and aromatic hydrocarbons is explained as due to intermolecular hydrogenation-dehydrogenation reactions.

(3) Of the ethylene reacting, 18.8% by weight was converted into isobutane. The isobutane obtained is considered to have originated in the polymerization of ethylene to 1- or 2-butene followed by isomerization to isobutene and this in turn is hydrogenated to isobutane by nascent hydrogen resulting from the simultaneous dehydrogenation of naphthenes to aromatics.

(4) The gaseous products contained hydrogen which represented 0.6% by volume of the ethylene reacting.

POLYMERIZATION OF PROPYLENE BY PHOSPHORIC ACID[1]

The polymerization of propylene by phosphoric acid was studied in detail by Ipatieff, Corson, Grosse, Komarewsky, Pines, Schaad, and White. During this study the effect of various promoters was investigated.

The study of the polymerization of propylene completely confirmed the hypothesis proposed by Ipatieff as an explanation of the polymerization of olefins. It also furnished much interesting information regarding the polymerization of other olefins, as well as the polymerization of mixtures of olefins.

The first experiment performed by Ipatieff and Pines on the polymerization of propylene in the presence of phosphoric acid was made under pressure in a rotating autoclave under the conditions described for the polymerization of amylene and ethylene.

TABLE 167

PROPERTIES OF PROPYLENE POLYMER FORMED IN THE PRESENCE OF PHOSPHORIC ACID

Fraction No.	B.P., °C.	G.	n_D^{19}	Analysis	
				% C	% H
1	82–149	2		84.9	15.1
2	149–166	8	1.4341	85.2	14.7
3	166–216	11	1.4440	85.7	14.4
4	216–221	3	1.4500	85.8	14.3
5	Above 221	4			

Thirty grams of phosphoric acid was placed in the glass liner of the bomb and propylene was pumped in until the pressure remained approximately constant at 10 atmospheres. The upper layer was distilled and investigated. The data in the preceding table show that under these conditions of polymerization, saturated hydrocarbons are present in the low boiling fraction. Further experiments on the polymerization of propylene were made at ordinary pressure, as well as at elevated pressure. Experiments at ordinary pressure were made by Corson in glass (Fig. 36) and copper apparatuses equipped with high speed stirrers. The copper apparatus could also be used for the polymerization of olefins under pressure (up to 30–40 pounds).

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[1] Ipatieff, Ind. Eng. Chem., 27, 1067 (1935).

Using 100% orthophosphoric acid as catalyst, propylene underwent polymerization at 130°, but at this low temperature the stirring had to be efficient in order to obtain satisfactory reaction velocity. The data obtained are summarized in the following table.

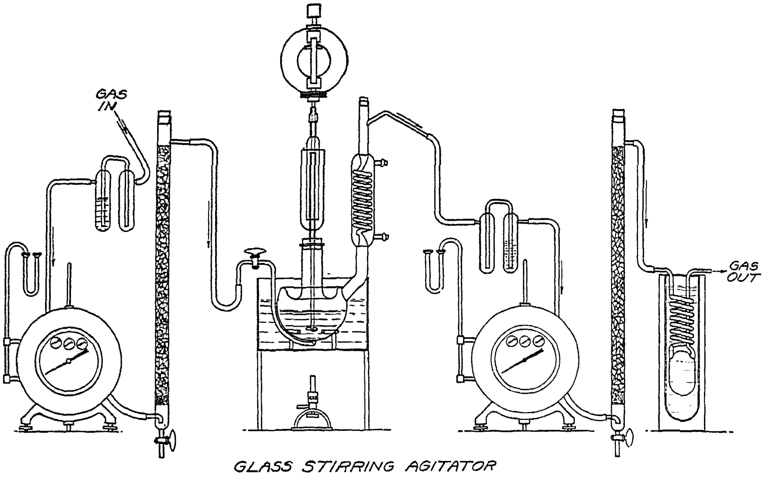

Fig. 36

TABLE 168

Polymerization of Propylene at Atmospheric Pressure and 130° C. in the Presence of 100% Orthophosphoric Acid

Expt. No.	T., °C.	Gas Rate, L./Hr.	Total Amount of Gas Processed, Liters	Contact Time, Seconds	% Conversion of Propylene Passed
1	130	4.55	46	1200	71
2	125	4.55	60	1200	49
3	130	8.50	74	700	63
4	130	7.10	124	850	55
5	135	4.55	131	1200	83

Propylene was polymerized to a liquid product which distilled from 90 to 260° and consisted entirely of unsaturated hydrocarbons. It was observed that the phosphoric acid did not decrease in catalytic activity; but that on the contrary, its activity increased with use. When 95% acid was used, instead of 100% phosphoric acid, polymerization of propylene occurred but more slowly. When the time of contact was 850 seconds, the extent of polymerization for the first six hours was 25%; for the following six hours, 40%.

The investigation of the polymerization of propylene included the study of all the reaction conditions, as well as the examination of the product. Ipatieff, Grosse, and White made experiments under pressure in a copper lined autoclave.

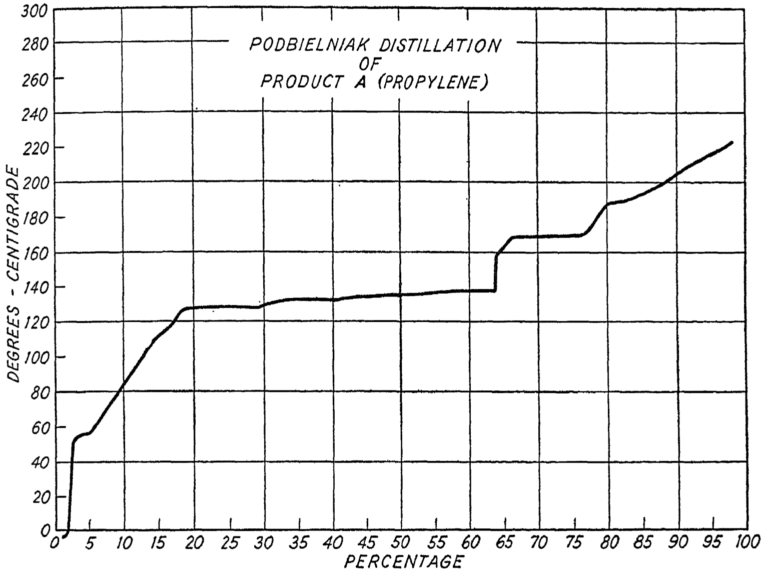

FIG. 37

The propylene used for the experiments was obtained from the Matheson Chemical Company and was 95% pure, 5% consisting of methane, ethane, and propane. This impurity did not interfere with the polymerization process.

Propylene under 50 atmospheres pressure was passed into the above-described bomb (containing 100% phosphoric acid) at 204°, while polymers and outlet gas (8.5 l./hr.) were withdrawn continuously. During 312 hours a total of 5960 g. of liquid polymer resulted, the polymer yield being 55% by weight of the propylene treated.

The propylene polymer[1] was distilled through a Podbielniak column (refer to distillation curve of product A).

TABLE 169

PROPERTIES OF PROPYLENE POLYMER FORMED AT 204° C. UNDER 50 ATMOSPHERES PRESSURE IN THE PRESENCE OF 100% ORTHOPHOSPHORIC ACID

Fraction No.	B.P., °C.	Cc.	% of Total	d^{20}	n_D^{20}	Observed Bromine No.	Theoretical Bromine No.
0	Gas	37.0	1.85				
1	25– 73	44.0	6.28	0.680	1.3930	158	190 C_6H_{12}
2	73–110	44.8	6.86	0.708	1.4093		
3	110–127	14.0	2.0		1.4159		
4	127–130	86.5	12.35	0.739	1.4222		
5	130–136	189.5	27.10	0.741	1.4247	136	127 C_9H_{18}
6	136–140	33.0	4.72	0.746	1.4278		
7	140–169	36.5	5.23	0.760	1.4350		
8	169–181	96.0	13.70	0.770	1.4380		
9	181–200	57.0	8.13	0.782	1.4443		
10	200–220	50.2	7.19	0.806	1.4549	91	92 $C_{12}H_{24}$
11	> 220	15.0	2.14		1.4966		

Fraction No. 0 was gas which was separated by the Podbielniak distillation from the liquid polymer. Analysis showed that it was 61% propylene, 1.9% propane, 2.6% isobutane, 2.8% butane, and 31.6% of gas not condensed at −160°.

Redistillation of the first fraction of the polymer (315 g.) gave the following results:

TABLE 170

REDISTILLATION OF LOW BOILING PROPYLENE POLYMERS

Fraction No.	B.P., °C.	Volume, Cc.	%	Bromine No.	n_D^{20}	d_4^{22}
0	Gas	1500	1.9			
1	36–59	20.5	96.8	151	1.3860	0.667
2	59–60.5	110.0		170	1.3930	0.677
3	60.5–63	111.0		182	1.3962	0.680
4	63.0–64.5	63.5		182	1.3987	0.683
5	Above 64.5	4.0	1.3		1.4150	

The data indicate that this fraction consisted of hexene and that it also contained some saturated hydrocarbon. The remaining fractions (2–11) reacted with potassium permanganate solution and with nitrating mixture. On treating them with sulphuric acid (96%) (1 volume of hydrocarbon to 2 volumes of sulphuric acid), they dissolved completely, forming a transparent solution which remained unchanged for a long period of time. Distillation of the upper layer showed that the amount of low boiling polymer was small; the part boiling at 127–136° (fractions 4, 5, and 6) represented about 50% of the total product. The properties and analysis showed that this fraction was *nonene*, C_9H_{18}. The other large fraction (8) corresponded to *dodecene*, $C_{12}H_{24}$.

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[1] The gas escaping from the polymerization apparatus was liquefied with solid carbon dioxide −78°. Most of the gas was liquefied. Analysis showed it to consist principally of propylene together with a small amount of saturated hydrocarbons.

A more detailed investigation of the polymerization product was made by Komarewsky. To decide as to the presence of saturated hydrocarbons in the first fraction (25–73°), it was treated with bromine, the halogen being added dropwise to the rapidly stirred, cold (0°) liquid until the appearance of a yellow color. The amount of original hydrocarbon was 29.4 g. and 39.6 g. of product was obtained. The product after washing with sodium hydroxide and drying with calcium chloride was distilled with the following results.

TABLE 171

Fraction No.	B.P., °C.	Wt., G.	n_D^{27}
1	40– 55	10	1.3725
2	55– 65	8.5	1.3745
3	65– 70	2.0	1.3810
4	150–180	11.5	1.4985
	Above 180	1.0	

Fraction 4 was pure *hexenedibromide*, $C_6H_{12}Br_2$. Fractions 1–3 which contained only traces of bromide were distilled over sodium and the distillate was investigated.

TABLE 172

Fraction No.	B.P., °C.	Product, G.	d^{20}	n_D^{20}	Analysis	
					% C	% H
1	50–55	7.5	0.630	1.3642	82.4	16.5
2	55–60	2.9		1.3680		
3	60–65	2.1	0.645	1.3714	82.8	16.4
4	65–69	0.6		1.3745		
Theoretical Values for C_6H_{14}					83.7	16.3

The fractions which did not react with bromine gave no reaction with potassium permanganate solution nor with nitrating mixture. According to analysis, they may be considered as consisting of hexane whose formation is explained by a side reaction in the polymerization process. (Refer to the chapter on the theoretical principles of catalysis.)

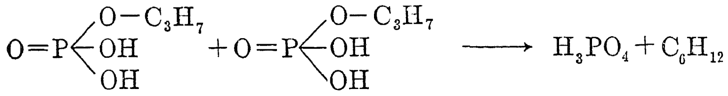
The fraction distilling at 130–150° (consisting chiefly of nonenes) was hydrogenated in order to obtain saturated hydrocarbons. Hydrogenation was performed at 240° under an initial hydrogen pressure of 100 atmospheres in the presence of a catalyst consisting of two parts of nickel oxide and one part of iron. The product, a transparent liquid distilling at 140–145° which did not react with potassium permanganate solution of nitrating mixture, was a mixture of isomeric nonanes.

Anal. Calcd. for C_9H_{20}: C, 84.3; H, 15.7. Found: C, 84.4; H, 15.6.

The data obtained warrants the following conclusions:

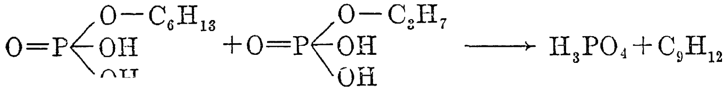
(1) Phosphoric acid (100%) is a good catalyst for the polymerization of propylene; one molecule of phosphoric acid can polymerize 90 molecules of olefin without decrease in activity.

(2) The polymerization of propylene may be considered as first producing a dimer, hexene:



$$O{=}P\begin{cases}O-C_3H_7\\ OH\\ OH\end{cases} + O{=}P\begin{cases}O-C_3H_7\\ OH\\ OH\end{cases} \longrightarrow H_3PO_4 + C_6H_{12}$$

Then the hexyl-ester of phosphoric acid probably reacts with the isopropyl-ester of phosphoric acid to give nonene:



$$O{=}P\begin{cases}O-C_6H_{13}\\ OH\\ OH\end{cases} + O{=}P\begin{cases}O-C_3H_7\\ OH\\ OH\end{cases} \longrightarrow H_3PO_4 + C_9H_{12}$$

Of course, two molecules of hexyl phosphoric acid will also give dodecene, $C_{12}H_{24}$. The fact that hexene is obtained in very small amount and that the chief product is *nonene* supports such an explanation.

In order to convince ourselves that the reaction proceeds through the intermediate formation of esters of phosphoric acid, a special experiment was made by Pines. Phosphoric acid was placed in a glass tube in a rotating autoclave and propylene was pumped in. The bomb was heated at 125° for several hours until the absorption of propylene ceased. At the end of the experiment the reaction product was a single layer system which contained the isopropyl ester of phosphoric acid. When this liquid was heated at 150° in the same rotating apparatus two layers were formed, an upper layer of propylene polymers previously described, and a lower layer of unchanged phosphoric acid which was capable of polymerizing more propylene.

Polymerization of Propylene by "Solid Phosphoric Acid"

Ipatieff, Schaad, and Corson [1] made many experiments on the polymerization of propylene and other olefins in the presence of so-called "solid phosphoric acid." Mixing phosphoric acid with various substances permits the preparation of contact masses rich in phosphoric acid which are solid at the temperature at which the polymerization of propylene and other olefins occurs. A whole series of such catalysts was prepared for this study. The experimental results showed that the velocity of the reaction depends to a considerable extent upon the method of preparing the catalyst, as well as upon the character of the solid material used as absorbent for the phosphoric acid. Polymerization (Table 173) was made in such a manner that propylene under a pressure of approximately 10 atmospheres passed through an iron tube filled with catalyst at a definite exit gas velocity. The range of reaction temperature was 150–250°. The velocity of the propylene entering the catalyst tube depended upon the activity of the catalyst. The exit gas was liquefied in carbon dioxide-acetone cooled receivers and the weight balance was calculated. With an exit gas velocity of approximately three liters per hour, and a catalyst sample of 40 to 90 g., the conversion into polymers was 80 to 93%. The catalysts were effective for long periods of time without change in activity and when their activity was lost they could be regenerated.

When propylene was diluted with gaseous paraffins, the rate of polymer formation was found to be proportional to the olefin content of the gas being processed.

According to special experiments made with Kurbatov, the catalytic action of such solid catalysts is due to the presence of phosphoric acid, and the polymerization reaction is proceeded by the formation of esters of phosphoric acid.

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[1] Ipatieff, Schaad, and Corson, unpublished results.

TABLE 173

Polymerization of Propylene by "Solid Phosphoric Acid Catalyst"

Catalyst No.	T., °C.	Press., Atms.	Time, Hrs.	Catalyst		Polymer, G.	Polymer, Cc./Hr./G. Catalyst	% Conversion into Polymer of Total Propylene Passed
				G.	Cc.			
1	250	9.25	296	47.0	63	3152	0.23	92.5
3	180	10.2	273	93.5	79.3	5672	0.22	93
7	177	10.4	69	80.0	61.5	2847	0.52	90
8	149	9.9	37	41.5	61.5	1711	1.11	91
12	150	10.4	69	75.5	61.5	3961	0.77	93
19	200	10.5	17.5	57.0	64.5	482	0.96	85
20	250	9.1	19.5	57.0	64.5	579	1.04	84

The reaction product from one of the experiments with the solid catalyst was distilled through a Podbielniak column (refer to distillation curve of product B). It is evident that this polymerization product very was similar to that obtained by polymeri-

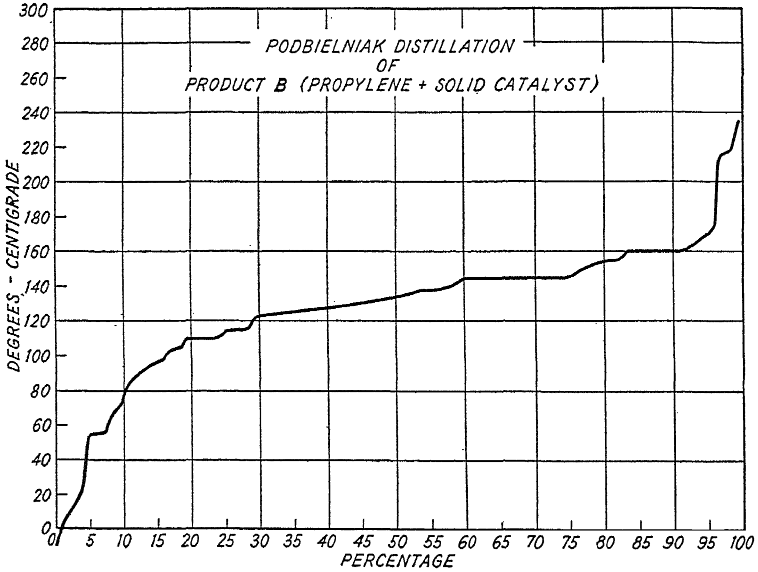


Fig. 38

zation with liquid phosphoric acid. Here, also, there was a small hexene fraction, a large fraction (about 55%) of nonene, and a small fraction of dodecene.

In order to determine whether saturated hydrocarbons were also present in the light fractions of the propylene polymer formed in the presence of "solid phosphoric acid" the fraction boiling at 25–73° was treated with bromine with cooling and stirring until the yellow color was permanent. From 30 g. of hydrocarbon taken, 59 g. of product was formed which after washing and drying, was distilled to obtain a fraction boiling at 40–80°. The remaining liquid, consisting of bromides, was distilled under diminished pressure. The fraction boiling at 40–80°, on redistillation over sodium, gave the following fractions: (1) 40–60° (1 g.), (2) 60–70° (4.2 g.). Neither of these fractions reacted with potassium permanganate solution or with nitrating mixture, and they evidently contained hexane, since the analytical figures were: C, 83.8%; H, 16.5%.

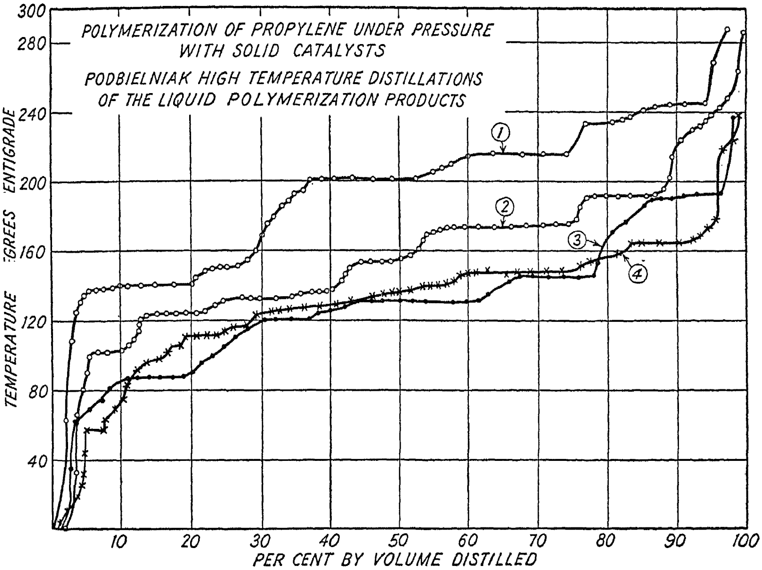


FIG. 39

Schaad, studying the influence of temperature and the activity of "solid phosphoric acid" catalysts upon the course of the polymerization of propylene found that the distillation curve of the polymers obtained by polymerization of propylene at 250° was lower than the distillation curve of the polymers obtained by polymerization of propylene at 200° (Fig. 39).

Distillation Curves 3 and 4 of polymer formed at 250° showed the presence of a considerable amount (about 50%) of nonene and only about 20% of material boiling above 160°.

Curve 2 corresponds to the distillation of propylene polymer made at 200°, and Curve 1 refers to the distillation of polymer made at 150°. It can be seen that with an increase in the temperature of polymerization there is a decrease in amount of high boiling fractions, and also that there are more polymers corresponding to dodecene. Due to the fact that in the two latter cases a solid catalyst of higher activity was used, a positive statement as to the influence of temperature cannot as yet be made, because of the numerous factors influencing the character of the resulting polymerization products.

The fraction containing the bromides distilled almost completely at 65–80° under 6 mm. pressure, and according to its properties and analysis was hexylene bromide, $C_6H_{12}Br_2$.

The second fraction distilling at 140–160° and corresponding to nonene was subjected to hydrogenation in the presence of nickel oxide and iron under pressure (initial hydrogen pressure, 100 atmospheres) at 200–210° for 12 hours. The colorless liquid obtained distilled at 140–150° and, according to its analysis and its properties, consisted of a mixture of nonane isomers. Thus, "solid phosphoric acid" catalysts polymerize propylene in a manner similar to liquid phosphoric acid.

Polymerization of Propylene under Pressure in the Presence of Phosphoric Acid and Promoters

Polymerization starts at lower temperatures in the presence of 89% orthophosphoric acid containing 10% by weight of various metallic salts and oxides than it does with acid alone. These experiments were made in a rotating autoclave containing a glass liner.

Thus even at 120°, within 10 hours, 25% of the propylene charge polymerized to form an upper layer consisting of liquid polymers distilling from 50 to 180°, and another 25% of the propylene charged produced isopropyl phosphates, which when distilled with steam gave equal parts of isopropyl alcohol and hydrocarbons. The reason for the formation of liquid polymers in the presence of promoters is explained by the catalytic action of the latter upon the decomposition of esters of phosphoric acid (see below).

Polymerization of Butenes by Phosphoric Acid

Ipatieff and Corson[1] conducted many experiments on the polymerization of the isomeric butenes. Corson[2] constructed an apparatus for obtaining pure butenes which permitted the preparation of large quantities of these olefins in a short time and with very little attention necessary (Fig. 40). A butyl alcohol was dropped from a constant-feed burette into a copper or a glass tube filled with activated alumina at 427°. The butene passed through a reflux condenser which retained water and undecomposed alcohol, and then through a calcium chloride drying tower, after which it was condensed in a receiver cooled with solid carbon dioxide and acetone. The liquefied olefin was stored in small iron cylinders.

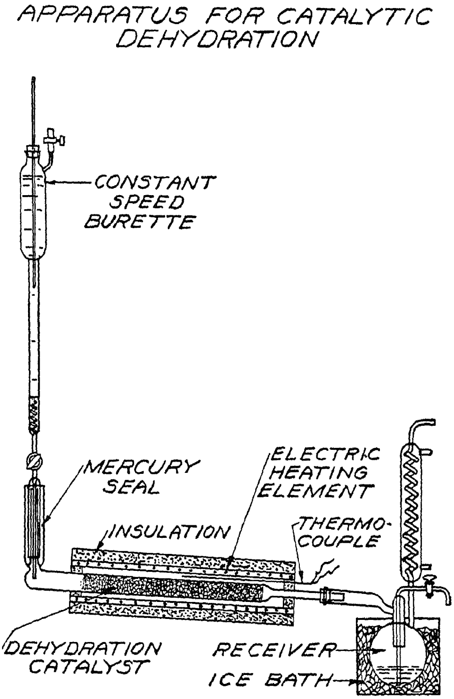


Fig. 40

All butenes obtained in this manner were analyzed by the low temperature fractional distillation method of Podbielniak. According to these distillation curves (Figs. 42, 43, 44) the butenes had the following composition:

The *1-butene* obtained from normal butanol (which distilled within a range of 0.5°) by decomposition with alumina contained neither isobutene nor 2-butene; it distilled completely at −5°.

The *2-butene* prepared from 2-butanol distilled from −5° to +2° and was therefore a mixture of 1- and 2-butene. This mixture of butenes was formed by the removal of water from the secondary butanol (distilling over a range of 0.5°) in two ways:

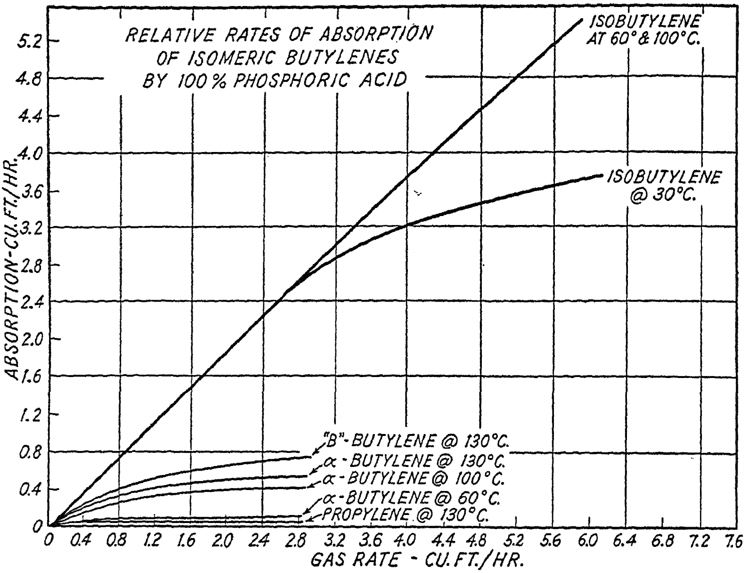
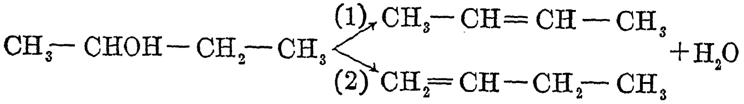


Fig. 41



$$CH_3-CHOH-CH_2-CH_3 \left\langle \begin{array}{l} \xrightarrow{(1)} CH_3-CH=CH-CH_3 \\ \xrightarrow{(2)} CH_2=CH-CH_2-CH_3 \end{array} \right. + H_2O$$

The *isobutene* prepared from isobutanol[1] was distinguished by a high degree of purity; it distilled completely at −6°.

Each isomer of butene was separately polymerized by phosphoric acid at ordinary pressure. The different butenes were passed through the apparatus (glass or copper) at definite rates, and the unabsorbed gas was condensed in a receiver cooled with solid carbon dioxide and acetone. The liquid polymers were discharged from time to time without dismantling the equipment, leaving the phosphoric acid in the apparatus until the end of the experiment (sometimes for 15 days).

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[1] Thus, the method proposed by Ipatieff as early as 1902 for obtaining olefins by catalytic decomposition of alcohols under the influence of alumina makes possible the production of substantially pure olefins in many cases. It has been shown that the isobutene obtained from isobutanol is practically pure. 1-Butene could not be obtained because of the difficulty in procuring the normal butanol at that time. The experiments of Corson and Pines have confirmed the purity of 1-butene and isobutene, but the impurity of the 2-butene is explained not by isomerization under these conditions, but by the removal of water in two ways.

The experiments showed that 85–89% phosphoric acid is a weak catalytic agent for the polymerization of butenes, and that 100% phosphoric acid is much more active.

The relative speeds of absorption of the different butenes were determined. Fresh acid was used for each olefin (Fig. 41). Isobutene showed the greatest reactivity; ethylene, the least.

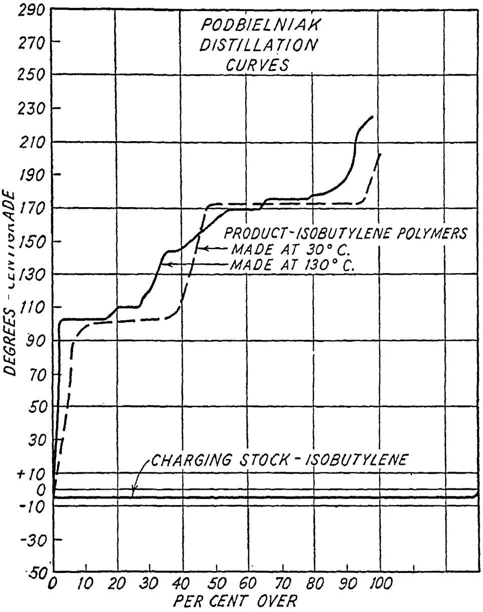

Fig. 42

The polymerization products of the individual butenes are similar, that is, they are mixtures of isomers which, although having different structures corresponding to the various butenes, reflect these differences but slightly in the general properties of the product.

In the case of isobutene (Fig. 42), three different temperatures, 30°, 60°, and 130° were employed. The product obtained at 30° contained only two individual polymers, namely, diisobutene [1] and triisobutene. The product formed at 130° contained about seven individual compounds comprising dimers and trimers. The higher the polymerization temperature, the greater the number of isomers formed, either due to isomerization or to removal of the elements of phosphoric acid from the intermediate esters in different ways.

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[1] It should be noted that phosphoric acid is an excellent catalyst at low temperature for the preparation of diisobutene from isobutene and that this reaction may be recommended for obtaining large amounts of diisobutene. The production of diisobutene by polymerization with sulphuric acid and zinc chloride gives smaller yields. Hydrogenation of diisobutene under pressure in the presence of nickel oxide readily yields pure isooctane.

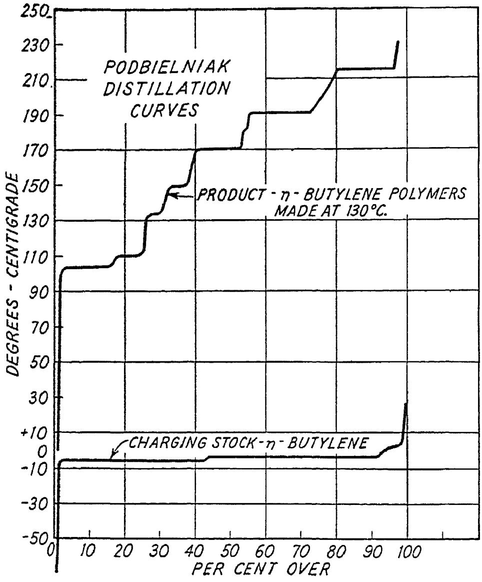


FIG. 43

The analytical data obtained are given in the following table.

TABLE 174

PROPERTIES OF THE POLYMERS FORMED FROM ISOBUTENE AT 130° IN THE PRESENCE OF 100% PHOSPHORIC ACID

Fraction No.	B.P., °C.	Volume, %	n_D^{28}	d_4^{25}	Observed Bromine No.	Calcd. Bromine No.	Analysis, % C	H	Calcd.
0	0- 42	2							
1	42-102	1							
2	102-103	14	1.4108	0.712	140				
3	103-110	4	1.4166	0.726		C_8H_{16}	85.3	14.3	C—85.7
4	110-112	7			147	143			H—14.3
5	112-122	3	1.4202	0.732					
6	122-144	5			118				
7	144-152	7	1.4270			$C_{12}H_{24}$	85.6	14.2	
8	152-161	7			82	95			
9	161-169	15	1.4320	0.760					
10	169-175	5							
11	175-178	14	1.4340	0.764		$C_{16}H_{32}$	85.3	14.1	
12	178-186	6			91	79			
13	186-220	5	1.4440						
14	220-227	4							

Data regarding the polymerization of 1-butene are presented graphically in Fig. 43, and numerically in the following table.

TABLE 175

PROPERTIES OF THE POLYMERS FORMED FROM 1-BUTENE AT 130° IN THE PRESENCE OF 100% PHOSPHORIC ACID

FRACTION No.	B.P., °C.	VOLUME, %	d_4^{25}	n_D^{25}	OBSERVED BROMINE No.	CALCD. BROMINE No.
0	0– 50	4				
1	50–102	2	0.702	1.4098	154	C_8H_{16}
2	102–110	13	0.727	1.4160	150	143
3	110–112	7	0.732	1.4188	152	
4	112–128	3	0.740	1.4252	128	
5	128–148	5	0.751	1.4306	117	$C_{12}H_{24}$
6	148–158	5	0.763	1.4330	105	95
7	158–174	5		1.4348	101	
8	174–175	15	0.774	1.4390	98	$C_{16}H_{32}$
9	175–190	13	0.784	1.4432	93	72
10	190–192	7	0.801	1.4510	59	
11	192–213	14				
12	213–230	7				

The polymerization product of the "2-butene" obtained from secondary butanol was a mixture of the polymerization products of 1-butene (40%) and 2-butene (60%).

The data are represented graphically in Figure 44, and numerically in Table 176.

TABLE 176

PROPERTIES OF POLYMERS FORMED FROM 2-BUTENE AT 130° IN THE PRESENCE OF 100% PHOSPHORIC ACID

FRACTION No.	B.P., °C.	VOLUME, %	d_4^{25}	n_4^{23}	CALCD. BROMINE No.	THEORET. BROMINE No.
0	0–102	6				
1	102–103	9		1.4125		C_8H_{16}
2	103–113	11	0.727	1.4175	139	143
3	113–134	3	0.734	1.4200		
4	134–140	5	0.740	1.4235		
5	140–148	5	0.748	1.4276		
6	148–170	7	0.756	1.4300		
7	170–174	5	0.764	1.4335		$C_{12}H_{24}$
8	174–184	15	0.771	1.4375	93	95
9	184–193	14		1.4410		$C_{16}H_{32}$
10	193–206	7	0.804	1.4490	69	72
11	206–242	13		1.4555		

In order to illustrate the catalytic life of phosphoric acid (100%) the following data are cited for the polymerization of 1-butene at 130°. With a gas rate of 14 liters per hour through 100 cc. of liquid phosphoric acid, 10,300 cc. of liquid polymer was obtained.

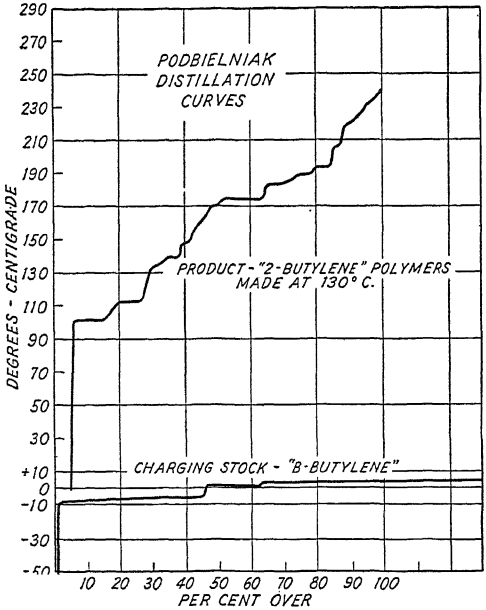


Fig. 44

Thus, one molecule of phosphoric acid polymerized 74 molecules of 1-butene. The experiment could have been continued longer since the catalyst was still active.

Polymerization of an Olefin Mixture

In studying the polymerization of olefins it was noted that propylene in the presence of butenes begins to polymerize at a lower temperature than when alone.[1] This observation on the polymerization of propylene in the presence of butene is new and has been investigated quantitatively.

When a mixture of propylene and butenes [2] was polymerized in the presence of a solid phosphoric acid catalyst at 150° and 10 atms. pressure, conditions under which propylene will polymerize alone, a product was obtained, the Podbielniak distillation of which is shown in the following curve.

[1] Ipatieff, Ind. Eng. Chem., 27, 1067 (1935).
[2] Ipatieff and Schaad, unpublished work.

A study of the above three curves leads to the conclusion that the product obtained from a mixture of olefins does not correspond to a mixture of the polymers formed from the separate olefins, under the same conditions.

In spite of the fact that the mixture of olefins contained considerably more propylene than butene, the distillation curve shows only a small fraction of the product corresponding to nonene which is the chief polymerization product when propylene is polymerized by itself. About 50% of the product boiled at 80–110°, corresponding to a mixture of isoheptene and diisobutene. On the basis of these data, the conclusion is obvious that the unstable esters of phosphoric acid originating from the addition of propylene and butene react with each other with a separation of phosphoric acid and the formation of a mixed polymer, isopropyl butene, C_7H_{14}, according to the following scheme.

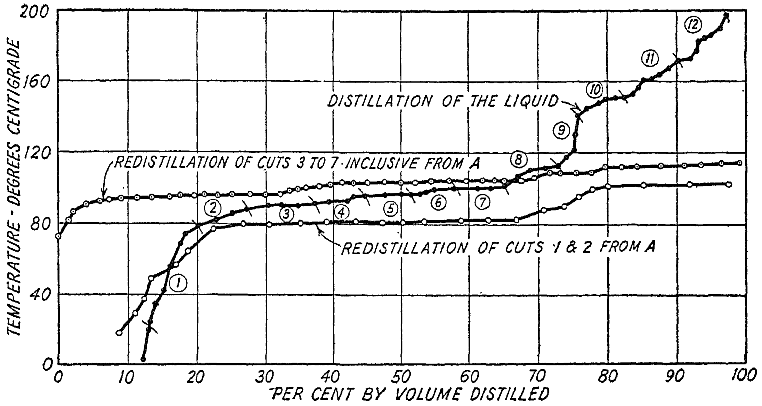
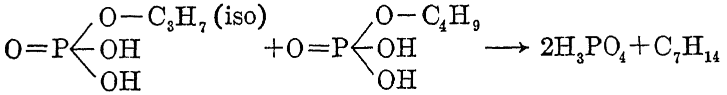


FIG. 45



$$O{=}P\begin{cases}O-C_3H_7\,(\text{iso})\\ OH\\ OH\end{cases} + O{=}P\begin{cases}O-C_4H_9\\ OH\\ OH\end{cases} \longrightarrow 2H_3PO_4 + C_7H_{14}$$

A high percentage of hexene is also formed. Further experiments in this direction are being made under various conditions in order to obtain quantitative results which will clarify the course of the polymerization of olefin mixtures.

Polymerization of an Olefin Mixture in the Presence of Phosphoric Acid with Sulphuric Acid as Promoter

While studying the polymerization of butenes, Ipatieff and Corson noticed that the addition of a small amount of sulphuric acid (5–10%) to the phosphoric acid greatly increased the velocity of polymerization.[1] Further, it was observed that phosphoric acid was able to catalyze the decomposition of esters of sulphuric acid upon slight heating (50–100°) to form alcohols and polymers of olefins.

To obtain a clear idea concerning the details of this reaction, Komarewsky experimented on the decomposition of diethyl sulphate and alkylated gasoline containing 1.4% sulphur (present in the form of sulphuric acid esters) by means of a small amount of phosphoric acid as a catalyst. Diethyl sulphate was dissolved in pure hexane (10% solution) and subjected to treatment with 10% by weight of phosphoric acid (89%) at 50–60°. The reaction was carried out in a flask under a reflux condenser and was complete in two hours. The entire product which separated from the acid distilled at 80° without decomposition and without leaving a residue. The reaction is represented by the following equation:

$$SO_2(OC_2H_5)_2 + H_3PO_4 + 2H_2O \rightarrow H_2SO_4 + H_3PO_4 + 2C_2H_5OH$$

The above solution of diethyl sulphate could not be distilled at ordinary pressure because it decomposed with evolution of sulphur trioxide and formation of a black residue in the flask. Alkylated products (containing sulphates) which could not be distilled because of decomposition, after treatment with phosphoric acid, gave a product which distilled without decomposition and which was nearly free from sulphur.

According to these data, it may be concluded that the addition of sulphuric acid to phosphoric acid may be useful in the polymerization of individual olefins as well as of mixtures of olefins because sulphuric acid forms esters readily and phosphoric acid causes their decomposition at a low temperature. Thus, for example, isobutene is polymerized by 100% phosphoric acid at 60° and at 95°, but not at 5°.[2] But, when 96% sulphuric acid was added to the 100% phosphoric acid, polymers distilling up to 225° were obtained in 95–100% yield. This product was superior to that formed by polymerization with sulphuric acid alone (66%) since only 50% of the latter distilled below 225°, the remaining liquid consisting of higher boiling polymers of isobutene.

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[1] This promoting effect of sulfuric acid was also studied with Grosse.

[2] Ipatieff and Corson, unpublished work.

Taking these facts into consideration, Komarewsky carried out a series of experiments on the polymerization of mixtures of olefins in the presence of 85% phosphoric acid to which was added 10% by weight of 96% sulphuric acid. The experiments were made at 150° in a rotating bomb equipped with a glass liner. Propylene and butene were liquified by solid carbon dioxide and acetone, and weighed amounts were taken. The amount of ethylene added was controlled by reading the pressure (knowing the volume of the bomb). The length of the experiments varied between 2 and 10 hours; the initial pressures exceeded 40 atmospheres, and the temperature varied from 130 to 150°. The data are presented in the following table:

TABLE 177

POLYMERIZATION OF OLEFIN MIXTURES IN THE PRESENCE OF 90% OF 85% PHOSPHORIC ACID AND 10% OF SULPHURIC ACID

EXPT. No.	COMPOSITION OF OLEFIN MIXTURE	T., °C.	TIME, HRS.	OLEFINS CHARGED, G.	OLEFINS RECOVERED AFTER THE REACTION, G.	OLEFINS ENTERING REACTION, G.	PRODUCT, % OF TOTAL DISTILLING UP TO 200°
126	Ethylene	150	9	33.36	22.02	11.34	97
	Propylene			39.49	2.32	37.17	
133	Ethylene	150	10	33.28	18.68	14.60	94
	Propylene			43.27	4.51	38.76	
135	Ethylene	150	10	40.86	21.08	19.18	95
	Propylene			61.30	10.60	50.70	
141	Ethylene	150	4.5	38.00	33.46	4.54	93
	Propylene			58.20	18.78	39.42	
122a	Ethylene	130	2	31.86	21.58	10.28	65
	Butylenes [a]			45.05	1.00	41.05	
122b	Propylene	130	2	38.51	2.91	35.60	65
	Butylenes			41.85	2.45	39.40	
121	Propylene	130	2	36.30	3.5	32.80	62
	Butylenes			44.33	2.0	42.33	
149	Ethylene	150	10	58.5	51.94	6.56	85
	Propylene			38.2	5.95	32.28	
	Butylenes			52.3	10.68	41.62	

utylene and 70% of 1- and
butylenes.

An experiment with ethylene alone showed that it did not polymerize to liquid product at 200° even with an increased amount of sulphuric acid in the mixture of phosphoric and sulphuric acids. Propylene alone, as indicated previously, requires a temperature of 150° or above for polymerization in the presence of phosphoric acid alone. An addition of 10% of sulphuric acid lowers the required reaction temperature, and at 130–140° 85% of the propylene is converted into polymers.[1] The butylenes polymerize completely into liquid products at 100°. The data presented in the table indicate that ethylene in a mixture of propylene and butylene undergoes polymerization in the presence of phosphoric promoted with sulphuric acid. In other words, propylene in the presence of butenes has the tendency to polymerize at a lower temperature than it does alone.

POLYMERIZATION OF OLEFINS BY METALLIC HALIDES

Polymerization of olefins under the influence of metallic halides attracted the attention of numerous investigators many years ago. The new factor of pressure, first proposed and applied to this polymerization reaction by Ipatieff in 1906–1911 greatly influenced the study of this process. Ipatieff and Routala [2] found that ethylene in the presence of zinc chloride polymerized at 250–270° under an initial pressure of 60–70 atmospheres. At the same time it was shown that freshly prepared aluminum chloride, when used in Ipatieff's high pressure iron apparatus, was also able to polymerize ethylene at ordinary temperature under an initial pressure of 60–70 atmospheres. According to our investigations the reaction product consisted of paraffin and naphthene hydrocarbons, and also unsaturated hydrocarbons which dissolved in sulphuric acid. These products were not examined further.

Fifteen years after our preliminary investigation, this reaction was applied to the commercial production of lubricating oils.[3] Stanley and Nash studied the polymerization of ethylene under pressure in the presence of aluminum chloride but they did not give sufficient data for a complete understanding of this complex reaction from a theoretical viewpoint. Comparing our investigations with theirs, we note that Stanley and Nash made the important observation that during the polymerization of ethylene under pressure in the presence of aluminum chloride, two layers were formed (similar to that in the Friedel and Crafts reaction on the alkylation of benzene). The upper layer contained chiefly saturated hydrocarbons having 10 to 40 carbon atoms. These saturated hydrocarbons corresponded to the formula C_nH_{2n}, and were in all probability, cycloparaffins. Only the lower boiling fractions contained paraffins. The lower layer consisted mainly of complex compounds formed between aluminum chloride and unsaturated hydrocarbons. These complex compounds were decomposed readily by water, giving unsaturated hydrocarbons with a lower hydrogen content than that required for olefins, C_nH_{2n}. It is assumed that perhaps they consist of olefins mixed with still more unsaturated hydrocarbons (possibly unsaturated cyclic compounds). The upper layer increased in amount with increase in reaction time and temperature.

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[1] Ipatieff, Grosse, and Corson found that phosphoric and sulfuric acids, alone or mixed, are not satisfactory polymerizing catalysts at ordinary pressure and relatively low temperature (ca. 50°) for propylene or for the mixture of olefins occurring in refinery gases.

[2] Ipatieff and Routala, Ber., *46*, 1748 (1913).

[3] Szayna, Przemysl Chem., *12*, 637 (1928); Stanley, J. Soc. Chem. Ind., *34*, 349–354 (1930); Nash, Stanley, and Bowen, J. Inst. Petroleum Tech., *16*, 830 (1930).

These investigations present insufficient data for the identification of the hydrocarbons present in the lower layer or for an understanding of the course of the reaction. The fact that Nash and Stanley conducted the polymerization of ethylene in the presence of petroleum ether at 10–15°, assuming that aluminum chloride does not act upon it below 100°, deserves special attention. Likewise, they assumed that the presence of hydrogen chloride has no influence upon the course of the reaction.

We studied in detail the alkylation of various classes of hydrocarbons by olefins in the presence of different catalysts, particularly aluminum chloride, and also the action of aluminum chloride upon various hydrocarbons and mixtures of hydrocarbons. This investigation gave convincing data as to the complexity of the reaction caused by the action of aluminum chloride upon ethylene. It was not simple polymerization. These data stimulated careful study of the action of aluminum chloride upon ethylene. A program was planned for investigation of the hydrocarbons forming the lower layer and determining the reasons for the formation of the upper layer.

In the chapter on theoretical principles of polymerization a preliminary hypothesis was proposed in regard to the formation of various hydrocarbons in the polymerization of olefins under the influence of halide catalysts, but only a systematic study of all the processes taking place as well as the character of the hydrocarbons formed would make it possible to really explain this complex reaction.

The investigation of the polymerization of olefins in the presence of metallic halides was carried out principally by Ipatieff and Grosse. This study is far from complete but the data already obtained deserve attention.

Polymerization of Ethylene by Aluminum Chloride

The polymerization of ethylene was made in the absence of solvent since experiments on the alkylation of hydrocarbons (refer to chapter on alkylation) showed that at temperatures below 100°, saturated hydrocarbons (paraffins and naphthenes) are alkylated by ethylene. In the presence of solvent, therefore, other products than polymers would be obtained.[1]

First the effect of hydrogen chloride upon the polymerization of ethylene was studied. Experiments showed that in the presence of freshly prepared and carefully sublimed aluminum chloride no polymer was formed from carefully dried ethylene at 32–36° under a pressure of 15 atmospheres in the absence of hydrogen chloride. The same aluminum chloride after the addition of dry hydrogen chloride caused the polymerization of dry ethylene under the same conditions. The charging of the bomb with aluminum chloride and hydrogen chloride was performed as follows: A definite amount of aluminum chloride (free from iron chloride) in a glass tube provided with a capillary opening was placed in the bomb. Air was carefully displaced from the bomb, which was then heated to 100° in order to sublime the aluminum chloride within thirty minutes. Afterwards, the bomb was slowly cooled and the residual hydrogen chloride (corresponding to 3 atmospheres) was pumped out. In the case of experiments in the presence of hydrogen chloride,[2] the bomb was filled with hydrogen chloride at 5 atmospheres pressure (3 g. of HCl). Carefully dried ethylene was added to 15 atmospheres pressure.

An insignificant increase in weight of the catalyst occurred as a result of traces of hydrogen chloride being retained by aluminum chloride. Another experiment on the polymerization of ethylene

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[1] It is necessary to realize that if the alkylation reaction does not begin immediately at the given temperature, it may start after a certain time has elapsed. It may be said, therefore, that "conjunct reactions" are dealt with in this case.

[2] Hydrogen chloride was liquefied in a high pressure bomb; when dry it can be stored without damage to the bomb.

TABLE 178

EFFECT OF HYDROGEN CHLORIDE ON THE POLYMERIZATION OF ETHYLENE IN THE PRESENCE OF ALUMINUM CHLORIDE

EXPT. No.	$AlCl_3$ WT., G.	T., °C.	PRESS., ATMS.	WT. INCREASE, G.	UPPER LAYER, G.	LOWER LAYER, G.	GASES, CC.	GAS ANALYSIS	
								% C_2H_4	% C_nH_{2n+2}
HYDROGEN CHLORIDE PRESENT									
133	24.68	32	15	23.91	22.60	1.30	3100	48.9	35.9 n = 2.74
HYDROGEN CHLORIDE ABSENT									
134	24.70	32	15	3.29		3.29	7200	96.6	1.2 n = 3.8

in the presence of aluminum chloride and HCl was made in a rotating autoclave (fitted with a glass liner) at ordinary temperature (about 25–30°) under an initial ethylene pressure of 20 atmospheres. The two layers were examined separately. In the following table the data obtained from the investigation of the upper layer are presented.

TABLE 179

PROPERTIES OF THE UPPER LAYER FORMED BY POLYMERIZATION OF ETHYLENE AT 25–30° C. IN THE PRESENCE OF ALUMINUM CHLORIDE AND HYDROGEN CHLORIDE

FRACTION No.	B.P., ° C.	PRESS., MM. Hg	WT., G.	VOL., CC.	n_D^{20}	d^{20}	ANALYSIS		CALCULATED	
							% C	% H	% C	% H
1	40– 50	760	0.89	1.09	1.3658					
2	50– 75	760	2.42	2.96	1.3733	0.677	83.72	16.32	83.61	16.39
3	75–100	760	4.60	5.63	1.3867	0.6835	83.93	16.03	(C_6H_{14})	
4	100–125	760	4.70	5.75	1.3987	0.7070	84.12	15.85	{84.10	15.90
5	125–150	760	2.85	3.49	1.4065	0.7215	84.43	15.68	(C_8H_{18})	
6	150–170	760	2.95	3.61	1.4138	0.7358	84.88	15.68		
1	50– 75	7	8.80	13.06	1.4235	0.7536	84.70	15.39	84.61	15.40
2	75–100	7	7.18	10.66	1.4328	0.7696	84.85	15.24	($C_{12}H_{26}$)	
3	100–125	7	6.69	9.93	1.4381	0.7832	85.31	15.05		
4	125–150	7	6.72	9.97	1.4470	0.7942	85.01	14.90	(C_nH_{2n})	
5	150–175	7	5.14	7.63	1.4524	0.8095	85.07	14.68		
6	175–200	7	3.57	5.30	1.4556	0.8292	85.30	14.63	85.61	14.38
7	200–225	7	2.79	4.14	1.4598	0.8296	85.37	14.45		
8	225–250	7	2.07	4.41	1.4634	0.8370	85.42	14.39		
9	250–255	7	0.87	1.09	1.4674	0.8482	85.50	14.36		
10	>255	7	2.19	3.25						

Eight per cent of each layer was lost during distillation. The first six fractions distilling up to 175° at ordinary pressure and the first two fractions boiling at 7 mm. did not react with potassium permanganate solution or with nitrating mixture. According to analysis and properties they consisted chiefly of paraffins. These eight fractions accounted for about 46% of the total upper layer.

In other experiments, the polymerization of ethylene was allowed to take place under the influence of aluminum chloride in the presence of hydrogen chloride which was introduced into the bomb twice, first under a pressure of 3 atmospheres and then under a pressure of 6 atmospheres. Polymerization under 20 atmospheres (maximum) pressure took place at 23–27°. Other conditions of the experiments were similar to those in the preceding experiment. The upper layer (311 g., 400 cc.) was distilled by Podbielniak's high temperature method, the data obtained being summarized in the following table:

TABLE 180

PROPERTIES OF THE UPPER LAYER FORMED BY POLYMERIZATION OF ETHYLENE AT 23–27° C. IN THE PRESENCE OF ALUMINUM CHLORIDE AND HYDROGEN CHLORIDE

FRACTION No.	B.P., ° C. @ 750 MM. Hg	WEIGHT, G.	d_4^{16}	n_D^{27}	MOL. WT.	ANALYSIS		CALCULATED	
						% C	% H	% C	% H
1	32– 80	16.1	0.6723	1.3714		82.56	16.11		
2	80–129	31.3	0.7052	1.3942		83.29	15.77		
3	129–179	20.7	0.7399	1.4111		83.69	15.37		
4	179–180	15.45	0.7509	1.4157				$C_{12}H_{26}$	
5	180–210	30.9	0.7606	1.4204	184	84.19	15.27	84.60	15.35
6	210–260	27.15	0.7842	1.4327				$C_{18}H_{38}$	
7	260–272	53.85	0.7961	1.4393	253	84.81	15.09	85.10	14.90
8	272–328	16.65	0.8140	1.4483				C_nH_{2n}	
9	328–368	31.85	0.8270	1.4565	339	85.60	14.61	85.62	14.38
10	368–372	19.60	0.8490	1.4602			14.04		
11	>372	27.0	0.9502	1.4680		84.41			

Nitrating mixture did not act upon the first six fractions, which evidently consisted of paraffins as indicated by the analyses. The remaining fractions reacted rather weakly with nitrating mixture; only the fraction boiling above 372° giving a vigorous reaction upon heating. The analyses and properties indicate that fractions 7 and 9 contain naphthenes, and that the fraction boiling above 372° contains unsaturated cyclic hydrocarbons.

The lower layer collected from several experiments was carefully decomposed with ice water in the presence of ether. After the ether was distilled, the residual liquid (264 g.) was distilled through a high temperature Podbielniak column. The results are given in the following table:

TABLE 181

POLYMERIZATION OF ETHYLENE IN THE PRESENCE OF ALUMINUM CHLORIDE AND HYDROGEN CHLORIDE

(Properties of the Liquid Obtained on Decomposing the Lower Layer with Ice Water)

FRACTION No.	B.P. @ 760 MM.	WEIGHT, G.	YIELD, %	d_{20}	n_D^{18}	Br_2 No.	ANALYSIS	
							% C	% H
1	175–212	25.75	10.3	0.8115	1.4530	177	86.4	13.36
2	212–236	23.40	9.0	0.8405	1.4711	201	86.77	12.97
3	236	10.20	4.0	0.8446	1.4746	183	86.65	12.94
4	236–264	25.20	9.7	0.8536	1.4774	162	86.72	13.01
5	264–292	20.90	8.0	0.8614	1.4807	165	86.75	12.96
6	292–336	34.20	12.8	0.8686	1.4843	152	86.87	13.01
7	336–350	27.80	10.3	0.8756	1.4875	144	86.73	12.95
8	350–392	18.80	7.0	0.8705	1.4897	148	86.75	12.79
9	>392	77.60	29.0	0.8998	1.5048			

The analytical data show that the hydrocarbons of the lower layer consisted of a mixture of unsaturated cyclic hydrocarbons. In order to determine the character of these hydrocarbons, the first fraction (b.p., 175–212°) was hydrogenated with nickel oxide at 260–270° under an initial hydrogen pressure of 100 atmospheres. Since the product from the first hydrogenation reacted slightly with nitrating mixture it was hydrogenated again, the temperature being 280–300°. The product was a colorless liquid upon which the nitrating mixture had little or no effect. It distilled at 174–213°; n_D^{20}, 1.4394.

This hydrogenated hydrocarbon on treatment with sulphuric acid (96%) at 0° remained unchanged in volume. It decreased in volume by 5% when treated with fuming sulphuric acid (15% SO_3). The hydrocarbon remaining after treatment with fuming sulphuric acid was entirely stable to nitrating mixture.

Anal. Found: C, 85.52%; H, 14.58%; n_D^{20}, 1.4366.

These data are evidence for the presence of naphthenic hydrocarbons, perhaps $C_{14}H_{28}$. At the present time, we are unable to state definitely whether the naphthene has a five-membered or a six-membered ring, or a combination of these rings. Dehydrogenation, according to the method of Zelinsky gave no definite results but since the naphthene was formed by hydrogenation of a hydrocarbon boiling at 175–212°, it may be a cyclic hydrocarbon with two double bonds either in a ring or in side chains.

Investigation of fraction 4 boiling at 236–264° led to similar conclusions. This fraction was hydrogenated in cyclohexane solution under pressure in the presence of nickel oxide at 255–280° (maximum pressure, 181 atmospheres) for 14 hours. The colorless product obtained after treatment with fuming sulphuric acid (15% SO_3) distilled at 230–275°. Its analysis and properties were as follows: C, 85.53%; H, 14.37%; n_D^{20}, 1.4568; d_4^{23}, 0.8286; molecular weight, 222.

The product did not react with nitrating mixture and according to its properties it should be a naphthene. Dehydrogenated over palladium, it gave a liquid (n_D^{20}, 1.4588) which reacted energetically with nitrating mixture and which was stable for two minutes with potassium permanganate solution. It may be possible that this naphthene had a six-membered ring.

Polymerization of Ethylene by Zirconium Chloride

Zirconium chloride [1] was prepared from its oxide by means of phosgene and it was purified by sublimation so as to produce a powder. Thirty atmospheres pressure of ethylene was pumped into the high pressure apparatus containing 12.3 g. of zirconium chloride. Polymerization took place even at 200° and after heating for five hours the pressure had decreased to 6.5 atmospheres. At the end of the reaction the zirconium chloride had acquired a brownish color and had increased in weight to 20.2 g. There was a transparent hydrocarbon layer above the catalyst which was separated, washed, and dried. Data from the investigation of this material are presented below.

TABLE 182

PROPERTIES OF ETHYLENE POLYMERS FORMED UNDER PRESSURE AT 200° C. IN THE PRESENCE OF ZIRCONIUM CHLORIDE

FRACTION No.	B.P., ° C.	YIELD, %	n_D^{20}	TEST WITH POTASSIUM PERMANGANATE	TEST WITH NITRATING MIXTURE
1	25–100	76.2	1.3749	No reaction	No reaction
2	100–200	17.9	1.4126	Weak reaction	Weak reaction
Residue	>200	5.9	1.5073		

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[1] Ipatieff and Grosse; it should be recorded that Grosse originally proposed the investigation of the catalytic action of zirconium chloride, thorium chloride, beryllium chloride, etc.

Analysis of the gas showed that it contained 75% of ethylene and 25% of paraffins. Calculation indicates that one molecule of zirconium chloride polymerized 13.7 molecules of ethylene.

Preliminary experiments were made with other metallic chlorides, the data obtained being presented in the following table:

TABLE 183

ACTION OF METALLIC CHLORIDES ON ETHYLENE AT 300° C. UNDER 30 TO 40 ATMOSPHERES INITIAL PRESSURE

CATALYST	T., ° C.	TIME, HRS.	INITIAL PRESS. OF C_2H_4, ATMS.	MAXIMUM PRESS., ATMS.	WEIGHT CATALYST, G.	WEIGHT CHANGE OF CATALYST, G.	B.P., ° C. OF POLYMERS	YIELD, %	ANALYSIS OF RESIDUAL GAS	
									C_2H_4	C_nH_{2n+2}
$ThCl_4$	300	2.5	30	53	13.97	8.68	60-210	49.0	90.0	8.0
$BeCl_2$	300	15	30	53	2.65	5.78	45-300	85.0	91.0	8.5
$MgCl_2$	300	8	40	94	23.7					
$CaCl_2$	300	22	30	60	36.0					
LiCl	300	8	30	57	24.8				95.4	2.1
NaCl	300	9	31	65	50.2				93.4	4.1
KCl	300	8	31	65	50.0				95.0	1.6
KBr	300	8	31	67	50.1				91.2	6.2

These preliminary experiments indicate that only thorium and beryllium chlorides are able to polymerize ethylene under the conditions described. Thorium chloride gave a large quantity (51%) of high boiling products, all fractions of the polymerization product being of an unsaturated character. Beryllium chloride is distinguished by the fact that it gave saturated hydrocarbons almost exclusively, a considerable amount of which being low boiling hydrocarbons.

Polymerization of Propylene by Aluminum Chloride

Aluminum chloride, as is well known, is a good catalyst for the polymerization of propylene. We studied the polymerization of propylene under moderate pressure (10–15 atmospheres) at ordinary temperature, and found that aluminum chloride was a true catalyst. In one of the experiments 136 g. of propylene was polymerized by 3.2 g. of aluminum chloride; i.e., one molecule of the latter polymerized 135 molecules of propylene. The reaction product was a homogeneous red liquid which separated into two layers on standing. The upper layer which constituted two-thirds of the total volume, was a yellow, viscous oil. The lower layer resembled the one obtained in the polymerization of ethylene except that it was more viscous. It was separated from the upper layer with difficulty. Both layers were treated with water to remove aluminum chloride. The upper layer contained about 5% of aluminum chloride which was removed completely by the water treatment.

The gas remaining after the polymerization of the ethylene contained a small amount of paraffins which, in all probability, consisted of ethane and propane. In one of the experiments, only 1.6 liters of gas (60% paraffins) remained after the polymerization of 108 g. of propylene. Fractional vacuum distillation of 76 g. of the upper layer separated the product into 6 fractions the properties of which are summarized in the following table.

TABLE 184

PROPERTIES OF THE UPPER LAYER FORMED BY THE POLYMERIZATION OF PROPYLENE UNDER 10–15 ATMS. PRESSURE

FRACTION No.	B.P., °C.	PRESS., MM. OF Hg	B.P., °C. @ 760 MM.	WEIGHT, G.	YIELD, %	COLOR	n_D^{22}	MOL. WT.	ANALYSIS	
									% C	% H
1	37–180 [a]	760	37–180	1.5	2.0	Colorless				
2	65–200	8–3.5	188–375	10.25	13.4	Pale yellow	1.4467	264	84.93	14.74
3	200–250	3.5	375–435	4.07	5.4	Pale yellow	1.4629	463	85.29	14.42
4	250 200	3.5 0.016	435–470	6.45	8.5	Yellow	1.4661			
5	200 260	0.016 0.033	470–530	9.16	12.1	Dark yellow	1.4704			
6	Residue		>530	44.45	58.4	Brown yellow	1.4779	1130	85.28	14.20

[a] The first fraction contained a small amount of ether due to the fact that the upper layer was extracted with ether after being washed with water.

All fractions consisted principally of olefins which decolorized potassium permanganate solution and reacted energetically with nitrating mixture. In the second fraction, paraffin hydrocarbons were also present.

The propylene polymer obtained in the presence of aluminum chloride contained a much larger proportion of unsaturated hydrocarbons than the polymer formed from ethylene under similar conditions. The reaction product also has a much higher boiling point, only 40% of it boiling below 500° C., while in the case of ethylene, the whole polymerization product distilled below 500° C.

The reaction velocities of polymerization are indicated in Figure 46. It is seen that the first three portions of propylene introduced into the autoclave polymerized within half an hour, and that the following portions required not more than one and one-half hours for their polymerization.

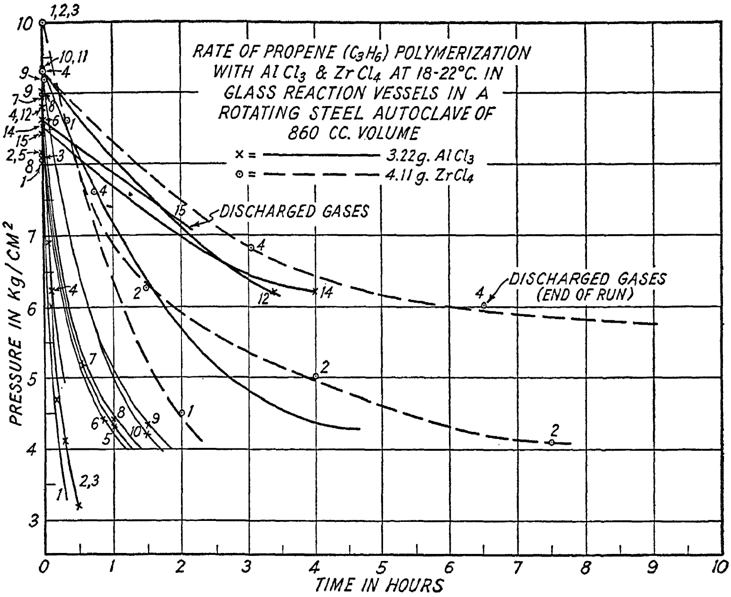

FIG. 46

Polymerization of Propylene by Zirconium Chloride

Zirconium chloride is very similar to aluminum chloride in catalytic action except that its velocity of polymerization is less as may be seen from Fig. 45. Inasmuch as one molecule of zirconium chloride polymerizes 240 molecules of propylene, or almost twice as many as aluminum chloride, it should be considered a better catalyst. Furthermore, zirconium chloride does not cause the formation of two layers in the polymerization of propylene as does aluminum chloride. The reaction product obtained at ordinary temperature was a homogeneous, transparent liquid with a pale yellow tinge, which did not separate into layers even on long standing. When the product was treated with water, an oil and a yellow precipitate containing all of the zirconium chloride (which is quite stable) separated. A very small amount of zirconium chloride (±0.1%) was present in the oil after being washed with water. When the yellow precipitate was treated with water, zirconium chloride dissolved and formed zirconium oxychloride which crystallized from the solution.

In view of the fact that zirconium chloride was being employed for the first time as a catalyst, it was necessary to make sure that the catalytic effect was not due to the presence of aluminum chloride. The zirconium chloride was decomposed by water, and sufficient fuming hydrochloric acid was added to produce a 25% solution of hydrogen chloride. Excess of phosphoric acid was added and the zirconium precipitated as pyrophosphate. Analysis showed that the zirconium chloride contained not more than 0.1% of aluminum chloride, an amount which could have no significance in the catalytic reaction.

About 8 liters gas was obtained. This gas obtained by polymerizing 118 g. of propylene consisted of about 60% propylene and 40% of saturated hydrocarbons (methane and propane). The liquid polymerization product was washed with water, dried, and distilled. The data are presented in the following table:

TABLE 185

Properties of Polymers Formed from Propylene under Pressure at Room Temperature in the Presence of Zirconium Chloride

Fraction No.	B.P., ° C.	Mm. Hg	B.P., ° C. @ 760 Mm.	Yield, %	n_D^{20}	d_4^{25}	Br No.	Analysis		Mol. Wt.
								% C	% H	
1	50-200	760	50-200	0.50	1.4222					
2	> 200	760	200-252	0.60						
	< 100	3.5								
3	100-200	3.5	252-375	7.12	1.4607	0.8170	46			
4	200-250	3.5	375-434	9.01	1.4696	0.8383	35	85.25	14.28	476
5	250	3.5	434-490	8.83	1.4726	0.8446	14			
	225	0.028								
6	225-260	0.028	490-520	17.3	1.4747	0.8503	18			
7	> 260	0.028	> 530	56.7	1.4793	0.8626	9	85.41	14.35	1250

All fractions were slightly yellow and soluble in benzene, ether, and hexane; the higher fractions were insoluble in alcohol. All fractions reacted energetically with potassium permanganate solution and with nitrating mixture. Analysis showed that they consisted of olefins, C_nH_{2n}. As seen from the table, about 60% of the polymers could not be distilled under the indicated reduced pressure. It is interesting to note that the residue was entirely colorless, while the fractions distilled off were slightly yellow. The residue from the preceding distillation was distilled under a pressure of 25×10^{-6} mm. Hg with the following results:

TABLE 186

HIGH VACUUM DISTILLATION OF HIGH BOILING PROPYLENE POLYMERS FORMED IN THE PRESENCE OF ZIRCONIUM CHLORIDE

FRACTION No.	B.P., °C.	AVG. PRESS., MM.	TIME, HRS.	WEIGHT, G.	% YIELD, TOTAL	n_D^{20}	d_4^{25}	Br No.
1	230–250	25×10^{-6}	35	13.11	45.00	1.4777	0.870	12
Residue				15.99	55.00	1.4802		

Thus, under high vacuum about 50% of the product may be distilled. The above fraction and the residue were colorless liquids.

Polymerization of Propylene by Tantalum Chloride

The polymerization conditions for propylene in the presence of tantalum chloride were similar to those used in the foregoing catalytic reactions. Air was evacuated from the bomb before pumping in the propylene; the reaction was run at 20–23°. The reaction product was a pale yellow, homogeneous liquid. An oily, solid residue containing the entire tantalum chloride remained at the bottom of the vessel. The tantalum chloride, when treated with water, formed a voluminous precipitate of tantalum hydroxide [$Ta(OH)_5$].

The liquid reaction product was dissolved in ether, washed with water, and analyzed.

TABLE 187

PROPERTIES OF POLYMERS FORMED FROM PROPYLENE AT 20° C. IN THE PRESENCE OF TANTALUM CHLORIDE

FRACTION No.	B.P., °C.	MM. Hg	B.P.,°C. @ 760 MM.	WEIGHT, G.	n_D^{20}
0	41–220	760		0.25	
1	75–150	3.5	230–314	3.3	1.4525
2	150–200	3.5	314–375	7.75	1.4611
3	200–250	3.5	375–435	8.1	1.4677
4	250–300	3.5	435–494	10.34	1.4710
5	300–316	3.5	494–514	3.54	1.4721
Residue	>316	3.5	514	8.11	1.4775

All fractions decolorized potassium permanganate solution and reacted energetically with nitrating mixture. In general, the product was similar to the polymerization product obtained with aluminum chloride and zirconium chloride, but it should be noted that tantalum chloride gave lower boiling products, 80% distilling below 500°. However, the activity of tantalum chloride is less than that of the other catalysts mentioned, one molecule of tantalum chloride polymerizing only 48 molecules of propylene.

THE POLYMERIZATION OF OLEFINS IN THE PRESENCE OF BORON FLUORIDE [1]

The olefins above ethylene are easily polymerized by boron fluoride [2] at room temperature and atmospheric or higher pressures in glass vessels. Ethylene is polymerized only if finely divided metals, especially nickel,[3] are present.

The olefins are polymerized into higher molecular weight mono-olefins in successive steps, as expressed, for instance, in the case of ethylene, by the following reactions:

$$C_2H_4 + nC_2H_4 \rightarrow (C_2H_4)_{n+1} \ (n=1, 2, 3, \text{etc.})$$

This is proven in the case of ethylene by the data presented in Table 188. The polymerization was effected in a rotating autoclave containing a glass liner. One hundred parts by weight of ethylene were polymerized in the presence of 4.5 parts BF_3 and 1.5 parts Ni-powder at 20–25° C. and 50 kg./cm.^{2} total pressure during 150 hours.

The chemical analysis, bromine numbers and molecular weight determinations, chemical tests and physical constants all consistently show that the different fractions are chiefly mono-olefins and that true polymerization of ethylene has taken place.

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[1] Ipatieff and Grosse, unpublished work.

[2] Butlerov and Gorianow, Ber., *6*, 561 (1873); Ann., *169*, 147 (1873); Butlerov, Ber., *9*, 1605 (1876); Ann., *189*, 44 (1877).

[3] Hoffmann and Otto, German Pat., 505,265, 512,959, 513,862; U.S. Patent, 1,811,130; Otto, Brennstoff-Chemie, *8*, 321 (1927); Hoffmann, Petroleum Times, *23*, 508 (1930).

The accelerating action of nickel was first noticed by Hoffmann and Otto but they did not realize it was a "conditio sine qua non" of the polymerization.

CHAPTER XII

ALKYLATION IN THE PRESENCE OF VARIOUS CATALYSTS

INTRODUCTION

The first experiments on alkylation of organic compounds were begun by the author together with Orlov and Razuvaev [1] in 1925, and concerned the alkylation of phenol in the presence of an alumina catalyst. Later, the alkylation of benzene by amylene in the presence of sulphuric acid was studied, the product obtained being amylbenzenes. Prior to these investigations the literature contained only two studies [2] which indicate that hydrocarbons containing a double bond may condense with aromatic hydrocarbons. Brochet showed that hexene and benzene in the presence of strong sulphuric acid gives hexylbenzene and dihexylbenzene. Brochet points out that this reaction is general for all olefins except in the case of amylene and benzene where he obtained only tarry products which could not be purified.

Experiments by Ipatieff and Pines showed that amylene reacts with benzene in the presence of sulphuric acid and gives good yields of mono-, di-, and triamylbenzenes. In addition, it was found that ethylene did not give satisfactory yields of ethylbenzene either at atmospheric or superatmospheric pressure, only traces of this product being obtained. On the other hand, alkylation with other gaseous olefins, such as propylene and butenes (carried out for the first time), gave excellent results. However, it should be noted that the dialkyl esters of sulphuric acid are obtained in appreciable amount in the alkylation reaction. In their presence, the reaction product cannot be distilled since decomposition takes place at about 120–130° and the product is lost.[3] These sulphuric esters can be removed from the reaction product by treatment with sulphuric acid (95–96%). It was also found that benzene can be alkylated by olefins in the presence of sulphuric acid containing a certain amount of phosphoric acid. Phosphoric acid decomposes dialkyl sulphates catalytically and the final product contains no alkyl sulphates at all and can be distilled without decomposition.

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[1] Ipatiev, Orlov, and Razuvaev, Bull. soc. chim., *37*, 157 (1925). Ipatieff, Orlov, and Petrow, Ber., *60*, 1006 (1927).

[2] Spilker, Ber., *23*, 3169 (1890). Brochet, Compt. rend., *117*, 115 (1893).

[3] Perhaps this circumstance may be the reason why Brochet was unable to obtain amylbenzene by the action of amylene on benzene in the presence of sulphuric acid.

After studying the alkylation of benzene by olefins in the presence of sulphuric acid, attention was focused upon the investigation of this reaction in the presence of other catalysts. It was discovered that phosphoric acid brings about the alkylation of certain hydrocarbons as well as phenols at ordinary and at superatmospheric pressure and at relatively low temperatures. Likewise, catalytic alkylation by means of perchloric acid under pressure was studied.

It was known from the literature that aromatic hydrocarbons can be alkylated by olefins in the presence of aluminum chloride.[1] Kurbatov, checking this reaction, found conditions under which one molecule of aluminum chloride converted 104 molecules of ethylene into alkylated benzenes. But the literature did not indicate the possibility of alkylating other classes of hydrocarbons by means of olefins in the presence of aluminum chloride. Halide derivatives of the hydrocarbon were used for the Friedel and Crafts reaction, the halide derivative alkylating the given hydrocarbon in the presence of aluminum chloride. Ipatieff [2] discovered that the saturated hydrocarbon hexane can be alkylated by ethylene at 60–70° at ordinary pressure in the presence of aluminum chloride to give alkyl substituted paraffins. This reaction gave within two hours a 10–14% yield of alkylated product. A blank experiment showed that hexane, under these conditions, undergoes a slight decomposition which, however, has practically no significance in considering the results obtained under the prescribed conditions. The first experiments on the alkylation of cyclohexane by ethylene in the presence of aluminum chloride gave negative results, while the alkylation of methylcyclohexane and methylisopropylcyclohexane gave positive results. Furthermore, by slightly increasing the reaction temperature, the amount of the catalyst, and the duration of the experiment, the alkylation of cyclohexane was accomplished at ordinary pressure.

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[1] Balsohn, Bull. soc. chim., (2), *31*, 539 (1879); Gustavson, J. prakt. Chem., *34*, 161 (1886); *ibid.*, *68*, 209 (1903).

[2] Ipatieff, Riverside (in publication).

The discovery of the possibility of alkylating paraffin hydrocarbons by olefins prompted a series of investigations concerning the action of aluminum chloride and other metallic halides, as well as their mixtures, upon various classes of hydrocarbons and types of hydrocarbon mixtures. The results of these experiments furnished a possible explanation of the reactions taking place and gave evidence of a special type of hydrocarbon alkylation which Ipatieff termed "destructive alkylation." This explanation also affords an approach to an understanding of the cracking process occurring in the presence, and in the absence of catalysts. The hypothesis explaining the alkylation of hydrocarbons, as well as the polymerization reaction related to it, is presented in the chapter on "Theoretical Principles for Catalytic Reactions."

Alkylation in the presence of aluminum chloride was studied by Ipatieff, Grosse, and Komarewsky, and alkylation in the presence of sulphuric acid and phosphoric acid was studied by Ipatieff, Corson, Pines, and Komarewsky.

The alkylation of aromatic hydrocarbons and phenols by olefins in the presence of sulphuric acid and phosphoric acid, as well as of metallic halides will be discussed first and a special section will be devoted to experiments on destructive alkylation.

ALKYLATION OF BENZENE BY OLEFINS IN THE PRESENCE OF SULPHURIC ACID [1]

Action of Amylene on Benzene

Experiments were made with Pines as follows: Three volumes of amylene (b.p., 34–38°) and 2 volumes of benzene in the presence of 7.5 volumes of sulphuric acid (92%) were either carefully mixed in a cylinder or stirred in a flask for 10 to 15 minutes at a temperature not exceeding 10°. The reaction product was allowed to stand in the cold for 12 hours during which time two layers formed. The upper transparent layer (3.8 volumes) was separated, washed with water, dried, distilled, and analyzed. None of the fractions decolorized potassium permanganate solution. It was evident that they contained mono-, di-, and triamylbenzenes.

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[1] Ipatieff, Corson, and Pines, J. Am. Chem. Soc., *58*, 919 (1936).

TABLE 189

Properties of Product Formed by Action of Amylene on Benzene in the Presence of Sulphuric Acid (92%) at 10°

Fraction No.	B.P., °C.	Amount, G.	n_D^{19}	Analysis		
				% C	% H	
1	43– 77	25				
2	77–104	14	1.4819			
3	104–204	9	1.4752	89.88	10.54	Monoamylbenzene
4	204–224	6	1.4769	88.13	12.44	
5	224–238	20	1.4820	87.57	12.80	Diamylbenzene
6	238–260	12	1.4841	87.15	12.66	
7	260–293	25	1.4852	86.82	12.75	Triamylbenzene
8	>293	7				

Action of Octene on Benzene

Seventy-two grams of octene (b.p., 121–124°) was added drop by drop to a mixture of benzene and 92% sulphuric acid. In the first experiment, the ratio of hydrocarbons was 1 mole of benzene and 1.04 moles of octene; in the second experiment, 1 mole of benzene and 2.2 moles of octene. The reaction was run 1.5–2 hours at 10–15°, after which the product was allowed to stand for about 12 hours. The upper layer was separated, washed, dried, distilled, and analyzed.

None of the fractions decolorized potassium permanganate solution, but all reacted with nitrating mixture and dissolved in concentrated sulphuric acid. As evident from the table, monooctyl benzene was the chief product obtained in Expt. No. 1; a mixture of isomers was present in the fractions boiling from 232 to 266°. In the second experiment, with octene in excess, dioctyl benzenes were obtained.

It was noted that the larger the amount of sulphuric acid, the smaller the quantity of sulphuric acid esters present in the upper layer. In other words, when a large amount of acid was used, the product did not require further purification and distilled without decomposition. Later it was established that for the reaction of olefins with aromatic hydrocarbons it was sufficient to use 1 molecule of the olefin for 2 molecules of benzene and 2 molecules of sulphuric acid. In this case, however, it was necessary to separate the product from the esters of sulphuric acid dissolved in it before the product could be distilled.

TABLE 190

ACTION OF OCTENE ON BENZENE AT 10–15° IN THE PRESENCE OF 92% SULPHURIC ACID

QUANTITIES OF MATERIALS USED	EXPT. NO. 1	EXPT. NO. 2
Octene, g.	72	71
Benzene, g.	43	20
Sulphuric acid, g.	265	275
Sulfuric acid after expt., g.	270	290

Properties of the Product

FRACTION NO.	B.P., ° C.	AMOUNT, G.		ANALYSIS		CALCULATED
				% C	% H	
PRODUCT FROM EXPT. NO. 1						
1	88–227	3				$C_6H_5C_8H_{17}$
2	227–232	6	1.4844			
3	232–238	17	1.4870	88.0	11.8	C—88.4%
4	238–239	28	1.4872			H—11.6%
5	239–243	16	1.4870			
6	243–266	12	1.4863			
7	266–277	3	1.4864			
8	277–329	3	1.4866			
9	329–357	5	1.4881			
PRODUCT FROM EXPT. NO. 2						
2	93–221	3				
3	221–310	2	1.4610			
4	310–327	6	1.4780			$C_6H_4(C_8H_{17})_2$
5	327–335	14	1.4831			
6	335–338	10	1.4855			C—87.4%
7	338–343	12	1.4852	86.9	13.0	H—12.6%
8	343–353	8	1.4839			
9	353	4	1.4819			
10	>353	2				

Action of Ethylene on Benzene

Experiments with ethylene and benzene in the presence of sulphuric acid showed that no ethylation occurred at ordinary pressure. Even under elevated pressure and at higher temperature alkylation took place only to an insignificant extent. In one of the experiments with an initial ethylene pressure of 58 atmospheres in an Ipatieff bomb containing 15 g. of benzene and 16 g. of sulphuric acid (92%), 10 g. of ethylene was absorbed in 4 hours. The fraction boiling at 100–200° gave 2 g. of liquid (n_D^{27}, 1.4894), which boiled at 116–143°. It did not decolorize potassium permanganate solution but it did react with nitrating mixture. According to its properties it was ethylbenzene but the yield of alkylated product was very small.

Action of Propylene on Benzene

Experiments on the alkylation of benzene by propylene at 0–5° were made with Corson. Propylene was passed into a stirring apparatus containing a mixture of 174 g. benzene and 183 g. of 96% sulphuric acid. The propylene was completely absorbed when passed into the mixture at a rate of 27 liters per hour. At the end of the reaction, during which 116 g. of propylene was absorbed, only 23 g. remained in the lower layer combined with sulphuric acid, the remaining 96 g. (81%) being in the upper layer combined with benzene. According to calculation it was found that the amount of propylene combined with the sulphuric acid was only 5% greater than that required for the formation of monopropyl benzene.

The upper layer was washed with water, dried, and distilled.[1] The data are presented in the following table:

TABLE 191

PROPERTIES OF PRODUCT FORMED BY ALKYLATION OF BENZENE WITH PROPYLENE IN THE PRESENCE OF SULPHURIC ACID AT 0–5° C.

FRACTION No.	B.P., °C.	AMOUNT, G.	ANALYSIS		CALCULATED	
			% C	% H	% C	% H
1	80– 82	4				
2	82–150	10			$C_6H_5C_3H_7$	
3	151–152	230	89.8	10.2	89.9	10.1
4	153–200	30				
5	201–204	50			$C_6H_4(C_3H_7)_2$	
6	205–206	200	88.5	11.1	88.8	11.2
7	207–222	20				
8	223–232	30			$C_6H_3(C_3H_7)_3$	
9	233–238	15	88.2	11.9	87.9	12.1

The residue in the distillation flask deposited needle-shaped crystals of tetraisopropylbenzene; m.p., 119°. None of the fractions contained unsaturated compounds or decolorized potassium permanganate solution. As may be seen from the above data, the reaction product consisted principally of mono- and diisopropylbenzene and a small amount of triisopropylbenzene.

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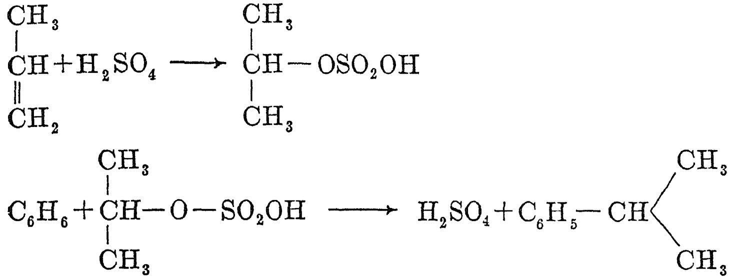
[1] Previous to distillation, it was necessary to remove the dipropyl sulphate, either by heating with phosphoric acid or by shaking with 4% by weight of cold 96% sulphuric acid.

The primary reaction proceeded according to the following scheme:



$$\begin{array}{l}CH_3\\ |\\ CH\\ \|\\ CH_2\end{array} + H_2SO_4 \longrightarrow \begin{array}{l}CH_3\\ |\\ CH-OSO_2OH\\ |\\ CH_3\end{array}$$

$$C_6H_6+\begin{array}{l}CH_3\\ |\\ CH-O-SO_2OH\\ |\\ CH_3\end{array} \longrightarrow H_2SO_4+C_6H_5-CH\begin{array}{l}CH_3\\ \\ CH_3\end{array}$$

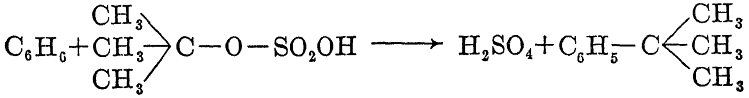
In all probability, the propyl ester of sulphuric acid formed *in statu nascendi* acts upon the molecule of benzene to alkylate it. It may also be possible that the benzene molecule is activated by sulphuric acid under the experimental conditions, thereby acquiring the ability to have its hydrogen atoms substituted by hydrocarbon radicals. Perhaps in the future the theory of chain reactions or conjugated reactions will assist in the clarification of this alkylation process.

Action of Butenes on Benzene

The alkylation of benzene by isobutene was first studied in the presence of 92% sulphuric acid. The experiments were made in 1932 by Corson under the conditions described above. To a mixture of 50 g. of sulphuric acid and 156 g. of benzene at 0° was added such an amount of isobutene that 20% of the benzene was alkylated. Mono- (35 g.) and diisobutylbenzene (65 g.) were obtained. No triisobutylbenzene was found among the reaction products. The liquid boiling at 177–180° (n_D^{30}, 1.4856) gave the following analytical figures:

Anal. Calcd. for $C_6H_5C_4H_9$: C, 89.5; H, 10.5. Found: C, 89.4; H, 10.1.

According to the analytical data, this product was a *tertiary-butylbenzene* originating in accordance with the following equation:



$$C_6H_6+\begin{array}{l}CH_3\\ CH_3\\ CH_3\end{array}\!\!>C-O-SO_2OH \longrightarrow H_2SO_4+C_6H_5-C\!\!<\!\begin{array}{l}CH_3\\ CH_3\\ CH_3\end{array}$$

The residue in the flask was an oil which crystallized on standing. Recrystallization from methyl alcohol yielded a solid which melted at 84–85°.

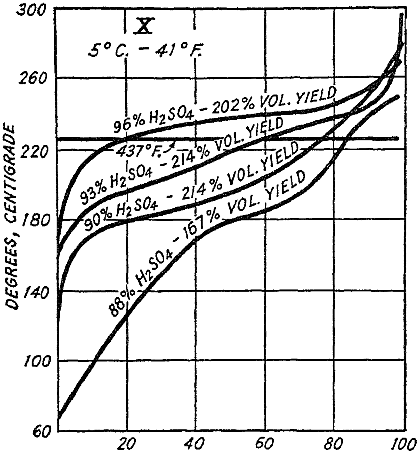


FIG. 47

Anal. Calcd. for $C_6H_4(C_4H_9)_2$: C, 88.4; H, 11.6. Found: C, 88.6; H, 11.7.

This product was therefore a *ditertiarybutylbenzene.*

Normal butylene (butene-1) alkylates benzene in the presence of sulphuric acid, the reaction beginning at 5°. The stronger the acid, the further the alkylation proceeds and the higher the boiling point of the product obtained.

Figures 47 and 48 show the relationship between the boiling point of the product, the strength of the acid used, and the reaction temperature.

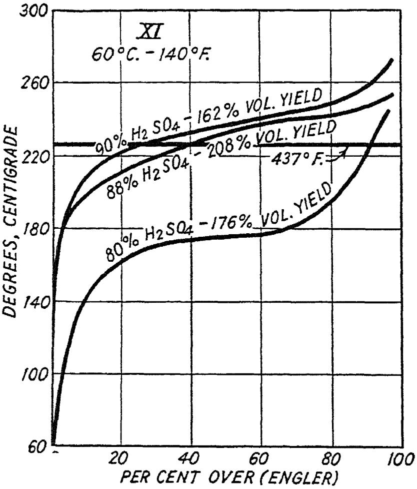


FIG. 48

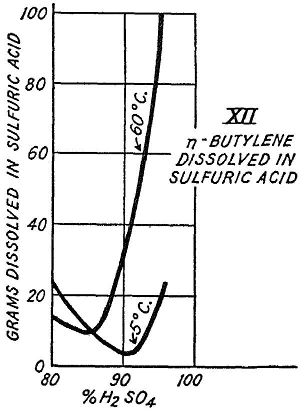
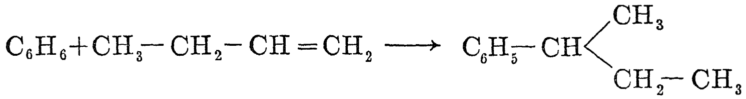


FIG. 49

Two types of reaction products were formed in these experiments, alkyl sulphates of sulphuric acid and alkylated benzenes. The distribution of butylene between benzene and sulphuric acid depends upon the concentration of the acid, its amount, the temperature, and also the structure of the olefin (Curve XII). The smallest formation of sulphate with n-butylene was obtained with 91% sulphuric acid. When the temperature was raised to 60°, the minimum amount of the sulphate was obtained with an acid strength of 85%. In the alkylation of benzene by n-butylene there are two main products, mono-butyl benzene (secondary) and di-butyl benzene (secondary).



$$C_6H_6 + CH_3-CH_2-CH=CH_2 \longrightarrow C_6H_5-CH\begin{cases} CH_3 \\ CH_2-CH_3 \end{cases}$$

Mono-butyl benzene (secondary) distills at 171–173°; d_4^{24}, 0.8577; $n_D^{15.5}$, 1.4928.

Anal. Calcd. for $C_{10}H_{14}$: C, 89.5; H, 10.5. Found: C, 89.4; H, 10.6.

The second fraction, boiling point 231–235°, was a new di-butyl benzene (secondary); d_4^{23}, 0.8545; n_D^{15}, 1.4905.

Anal. Calcd. for $C_{14}H_{22}$: C, 88.5; H, 11.6. Found: C, 88.1; H, 11.7.

ALKYLATION BY PHOSPHORIC ACID

After it had been established that phosphoric acid catalytically decomposes the esters of sulphuric acid, it seemed interesting to study the alkylation of benzene by olefins in the presence of sulphuric acid admixed with phosphoric acid. Experiments confirmed our expectations. The alkylation product did not contain sulphates and could be distilled without decomposition.

TABLE 192

B.P., °C.	YIELD, %	d_4^{20}	n_D^{27}	ANALYSIS		DATA FROM LITERATURE			
				% C	% H	% C	% H	d_4^{18}	n_D^{20}
80– 85	20		1.4804						
85– 95	38		1.4769			(Diisobutylene)			
95–108	42	0.738	1.4335	86.0	13.61	85.7	14.3	0.715	1.4090
108–150	55		1.4264						
150–170	60		1.4559			[Mono- (tertiary) butylbenzene]			
170–174	80	0.806	1.4617	85.7	12.12	89.5	10.5	0.867	1.4850
174–180	92		1.4602						
180–220	100		1.4615						

Corson then showed that phosphoric acid alone is able to alkylate benzene. The first example of this reaction was encountered in the study of the action of isobutylene upon benzene in the presence of phosphoric acid. Isobutylene, passed rapidly through benzene in the presence of 100% phosphoric acid at 60°, partly underwent polymerization and partly alkylated the benzene with the formation of mono- (tertiary) butylbenzene and di- (tertiary) butylbenzene. The reaction product was distilled and the fractions were analyzed.

Considering the properties of the fraction boiling at 170–174° it is evident that it represents a mixture in almost equal proportions of mono- (tertiary) butylbenzene and triisobutylene (see following data).

TABLE 193

PROPERTIES OF MIXTURE	50% TERTIARY BUTYLBENZENE 50% TRIISOBUTYLENE	
	CALCULATED	FOUND
C	87.6%	87.5%
H	12.4%	12.1%
n^{27}_{-}	1.458	1.462

In addition, the behavior of this fraction toward certain reagents showed that a mixture of olefins and aromatic hydrocarbons was present. The isolation of di- (tertiary) butylbenzene furnished conclusive proof of the alkylation of benzene by isobutylene in the presence of phosphoric acid. The distillation residue deposited crystals (4 g.) which were found to be identical in properties with di- (tertiary) butylbenzene obtained by the alkylation of benzene in the presence of sulphuric acid. Recent investigations on the alkylation of aromatic hydrocarbons in the presence of phosphoric acid showed us that under pressure one obtains exclusive alkylation of the benzene ring without the formation of polymerization products.[1]

ALKYLATION OF NAPHTHALENE AND FLUORENE IN THE PRESENCE OF PHOSPHORIC ACID

After the alkylation of benzene with olefins in the presence of phosphoric acid had been established by Ipatieff and Corson, experiments on the alkylation of naphthalene and fluorene in the presence of the same catalyst were made by Ipatieff and Komarewsky. Alkylation of naphthalene by propylene in the presence of

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[1] Ipatieff and Pines, Riverside (1933).

89% phosphoric acid was made under pressure in a rotating bomb; 40.2 g. of naphthalene, 37.8 g. of propylene, and 51.6 g. of 89% phosphoric acid being used. The reaction was allowed to proceed at 200° for 14 hours. A weight increase of 33.1 g. (after removal of the propylene) was obtained. The pressure maintained during the experiment did not exceed 15 atmospheres. The naphthalene which had not entered into the reaction was separated from the liquid product and the latter was distilled. The following fractions were obtained: (1) 120–190° (13 g.); (2) 190–260° (27 g.) (crystals to a great extent); (3) 260–280° (4.6 g.); (4) 280–290° (10 g.). Analyses of the last two fractions gave the following figures:

Anal. Calcd. for $C_{13}H_{14}$: C, 91.2; H, 8.8. Found: C, 91.1; H, 8.9. The hydrocarbon obtained was therefore *isopropylnaphthalene.*

When naphthalene alone was heated with phosphoric acid at 200°, it did not suffer any change and no liquid product was formed.

The alkylation of fluorene by propylene proceeded with still greater ease. The reaction took place at 120° under a pressure of 10–15 atmospheres; 26.8 g. of fluorene and 25.1 g. of propylene being heated in the presence of 25 g. of 89% phosphoric acid at 120° for 14 hours. The weight increase was 66 g. A fraction boiling at 310–330° (n_D^{27}, 1.6055) was separated in about 30% yield. Its analysis gave the following data:

Anal. Calcd. for $C_{14}H_{10}$: C, 92.3; H, 7.7. Found: C, 92.1; H, 8.0.

The product was therefore *isopropylfluorene.*

ALKYLATION OF AROMATIC HYDROCARBONS WITH ETHYLENE IN THE PRESENCE OF ZIRCONIUM CHLORIDE

Benzene was subjected to the action of ethylene in a rotating bomb in the presence of zirconium chloride and hydrogen chloride. Experiments made by Ipatieff and Grosse had shown that zirconium chloride behaves similarly to aluminum chloride, but the temperature must be maintained between 50° and 100°. As a result of these conditions, mono-, di-, tri-, tetra-, penta-, and hexaethylbenzenes were obtained.

One molecule of zirconium chloride can bring about the addition of 90 molecules of ethylene to benzene. In this respect it differs from aluminum chloride in the alkylation of benzene according to the data in the literature (Mulliken, Reid), but experiments made by Kurbatov [1] in this laboratory showed that under certain conditions one molecule of aluminum chloride can cause the addition of 104 molecules of ethylene to benzene.

TABLE 194

Weight Balance of the Reaction: T°, 50; $P_{\max}$, 20 Atms.

Before Reaction:		*After Reaction:*	
Zirconium Chloride	12.4 g.	Gas	900.0 cc.
Benzene	126.4	Upper Layer	169.6 g.
Ethylene Absorbed	58.0	Lower Layer	
Hydrogen Chloride	6.0	Hydrocarbon	14.8
Total	196.8 g.	Zirconium Chloride	12.4
		Total	196.8 g.

The gas consisted of approximately equal parts of ethylene and paraffins. The upper layer was a pale orange liquid. It contained no chlorine but showed traces of zirconium oxide. It was washed and distilled to give the following data.

TABLE 195

Alkylation of Benzene by Zirconium Chloride

Fraction No.	B.P., °C. @ 749 Mm.	Weight, G.	Yield, %	d_4^{20}	n_D^{27}	Action of Potassium Permanganate	Action of Nitrating Mixture
1	78 - 81.5	20.6	12.7	0.8615	1.4862	None	Energetic
2	81.5-139	66.9	41.0	0.8653	1.4902	None	Energetic
3	139 -187	56.9	34.9	0.8640	1.4914	None	Energetic
4	187 -220	8.0	4.9	0.8700	1.4934	After 1 min.	Energetic
5	>220	7.7	4.7	0.9004	1.5087	After 1 min.	Energetic
Loss		2.9	1.8				
Total		163.0	100.0				

Fractions 2, 3, and 4 were redistilled and separated into the following fractions: (1) 138–140°; (2) 180–182°. On the basis of their properties and analyses they were identified as ethylbenzene and diethylbenzene, respectively. Oxidation of the 140–141° fraction yielded benzoic acid.

The lower layer (27.1 g.) contained all the zirconium chloride and it was reused as catalyst for the alkylation of a fresh portion of benzene by ethylene.

[1] Unpublished work, Riverside.

TABLE 196

Weight Balance of the Reaction

Before Reaction:	
Lower Layer	27.1 g
Benzene	136.8
Hydrogen Chloride	6.0
Ethylene Absorbed	72.3
Total	236.2 g.

After Reaction:	
Gas (uncondensable)	56.0 cc.
Gas (condensed by carbon dioxide-acetone)	3.0 g.
Upper Layer	211.3
Lower Layer	22.9
Total	236.2 g.

The conditions of the reaction were the same as those in the preceding experiment. The gas remaining at the end of the reaction was pure ethylene. The Podbielniak distillation data of the upper layer are summarized in the following table:

TABLE 197

Alkylation of Benzene by Ethylene in the Presence of Zirconium Chloride (Old Catalyst Re-used)

Fraction No	B.P., °C. @ 747 Mm.	Weight, G.	Volume, Cc.	n_D^{26}	Action of Potassium Permanganate	Reaction Product
1	80– 81	62.3	61.4	1.4889	None	Benzene
2	81–140	44.7	53.5	1.4915	None	Ethylbenzene
3	140–188	33.9	37.0	1.4934	None	Diethylbenzene
4	188–224	17.1	16.0	1.4969	None	Triethylbenzene Tetraethylbenzene
5	224–242	17.0	20.0	1.5063	None	Pentaethylbenzene Hexaethylbenzene
6	Above 242	13.0	15.5	1.537	After 1 min.	Crystals, m.p., 128–129° separated

The results of these experiments show that the catalytic action of zirconium chloride is similar to that of aluminum chloride when used in the alkylation of aromatic hydrocarbons by olefins.

A preliminary investigation of the oil in the upper layer boiling above 242° indicated that it contained a certain amount of unsaturated compounds formed by the polymerization of ethylene with liberation of hydrogen. Its analysis (C, 89.4%; H, 10.9%) showed, however, that it was mainly a mixture of penta- and hexaethylbenzenes.

The lower layer was decomposed by water, and the oil floating on top (8.3 g.) was distilled; 7.5 g. of this oil distilled at 80° to 295° and was found to consist of benzene, ethylbenzene, triethylbenzene, and hexaethylbenzene.

ALKYLATION OF BENZENE BY ETHYLENE IN THE PRESENCE OF TANTALUM CHLORIDE

The conditions of this reaction were identical with those in the preceding experiments. One molecule of tantalum pentachloride brought about the reaction of 61 molecules of ethylene.

TABLE 198

WEIGHT BALANCE OF THE REACTION: T°, 50–75°; P_{max}, 20 ATMS.

Before Reaction:		*After Completion Reaction:*	
Tantalum Chloride	19.7 g.	Gas	320.0 cc.
Benzene	152.7	Liquid Product	237.5 g.
Hydrogen Chloride	7.0	Solid Product	
Ethylene Absorbed	98.8	Tantalum Chloride	19.7
		Hydrocarbon	15.0
Total	278.2 g.	Total	272.2 g.

A liquid layer and a dark red pasty mass were obtained. The latter was decomposed with water, giving a small amount of liquid hydrocarbons containing 0.15 g. tantalum oxide. The tantalic acid remaining was separated by decomposition with water in the form of an insoluble residue. The Podbielniak distillation data of the liquid product are presented in Table 199 on p. 665. Eight and two-tenths grams of hexaethylbenzene was obtained. Therefore, tantalum pentachloride is an active catalyst for the alkylation of benzene. The solid reaction product also consisted of alkylated benzenes and contained a very small amount of unsaturated hydrocarbons.

ALKYLATION OF PHENOLS BY ALUMINA

The alkylation of phenols was studied by Ipatieff, Orlov, and Rasuvaev[1] primarily in the presence of alumina. The phenol was heated with methyl alcohol and alumina in Ipatieff's high pressure apparatus at 440° for 24 hours under pressures up to

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[1] Ipatieff, Orlov, and Rasuvaev, Bull. soc. chim., *37*, 1576 (1925).

TABLE 199

ALKYLATION OF BENZENE BY ETHYLENE IN THE PRESENCE OF TANTALUM PENTACHLORIDE

FRACTION No.	B.P., °C. @ 748 MM.	WEIGHT, G.	d_4^{16}	n_D^{29}	ACTION OF POTASSIUM PERMANGANATE	REACTION PRODUCT
1	28– 80	1600 cc. gas 25° 748	0.8797	1.4858	None	Benzene
2	80–140	53.0	0.8704	1.4900	None	Ethylbenzene
3	140–182	8.2		1.4915		
4	182–188	32.5	0.8694	1.4915	None	Diethylbenzene
5	188–220	14.2		1.4941		
6	220–236	20.0	0.8823	1.4992	None	
7	236–276	9.5		1.5076		
8	>276	22.0				Hexaethylbenzene, m.p., 128–128.5°

200 atmospheres. The chief reaction product was an o-cresol, and there was also a very small amount of benzene and anisole formed. Meta- and para-cresols were not detected. Various explanations for this reaction may be given. It is possible that anisole is first formed, undergoing an isomeric transformation into o-cresol.

$$C_6H_5OH + CH_3OH \rightarrow H_2O{-}C_6H_5{-}O{-}CH_3$$

$$C_6H_5{-}OCH_3 \rightarrow C_6H_4CH_3(OH)$$

To test this hypothetical isomerization, anisole was heated at 440° under hydrogen pressure in the presence of alumina. Among the decomposition products a small amount of o-cresol was detected. Experiments also showed that phenol is alkylated when heated with ethyl alcohol in the presence of alumina and as a result ethyl phenol is obtained. But the yield of the latter is small.

Another explanation is based upon the formation of the methyl ester of the hydrate of aluminum oxide and in this case the phenol alkylation would be similar to alkylation by sulphuric acid and phosphoric acids.

$$AlO(OH) + CH_3OH \quad H_2O + AlO(OCH_3)$$

$$AlO(OCH_3) - \quad \rightarrow AlO(OH) + C_6H_4CH_3(OH)$$

Action of Propyl Alcohol on Phenol in the Presence of Alumina [1]

Our investigations showed that the action under superatmospheric pressure of methyl alcohol on phenol in the presence of alumina differs greatly from the reaction at ordinary pressure as studied by Briner, Sabatier and Mailhe, and others. Alkylation of phenol was observed in the case of methyl and ethyl alcohols and therefore it appeared interesting to study this reaction with other alcohols, e.g., propyl alcohol. According to previous experiments the formation of propyl phenyl ether and propyl phenol would be expected. Conducting the reaction at 380–400° for 12 hours under a maximum pressure of 125–130 atmospheres, the following products were obtained: propyl phenyl ether, alkylated phenols (among which were propyl phenol and its propyl ether) a considerable amount of n-propyl ether and naphthenic hydrocarbons.

The formation of naphthenic hydrocarbons was due to the removal of water from propyl alcohol and subsequent polymerization of the resulting propylene. The formation of dipropyl ether and propyl phenyl ether is readily understood on the basis of Ipatieff's [2] investigations. Thus, in the case of propyl alcohol, the alkylation of phenol proceeds in the same way as with other alcohols, propyl phenol [3] being formed.

These reactions take place under pressure. Experiments made at atmospheric pressure in which a mixture of 2 weight parts of propyl alcohol and 1 weight part of phenol was passed over alumina at 450–500° showed that propylene was practically the only product. There was only a very small amount of a brownish substance containing a trace of phenyl propyl ether, $C_6H_5—OC_3H_7$. Practically all of the phenol remained unchanged.

Two parts by weight of propyl alcohol, 1 part by weight of phenol, and 1/50 to 1/60 part by weight of alumina were used in the experiments. A temperature of 380–400° was maintained; the maximum pressure was 125 atmospheres, and the duration of heating was 8 to 12 hours. The capacity of the bomb was 1 liter and 330 cc. of liquid was charged. At the end of the reaction, the pressure had decreased to about 10 atmospheres and analysis of the residual gas gave the following figures: C_nH_{2n}, 30%; CO + CO_2, 5%; C_nH_{2n+2}, 60%. The unused portion of the gas was passed into bromine and the resulting bromide was found to be propylene bromide, b.p., 141–143°. The reaction product was a mobile liquid, slightly yellow in color, which separated into two layers, a lower aqueous layer and an upper oily layer. Fifteen hundred grams of upper layer was obtained which was washed with water and then with 10% sodium hydroxide to extract the phenols; 600 g. of an oil insoluble in sodium hydroxide resulted and 870 g. of phenols separated from the alkaline solution after acidification. The oil insoluble in sodium hydroxide was distilled and four fractions were collected: (1) 60–80° (26 g.); (2) 80–150° (principally 80–100°) (225 g.); (3) 150–200° (57 g.); (4) 80–200° at 10 mm. (270 g.). Redistillation yielded two principal fractions, one boiling at 88–91°, the other at 188–192°.

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[1] Ipatieff, Orlow, and Petrow, Ber., *60*, 1006 (1927).

[2] Ipatieff, Ber., *37*, 2986 (1904).

[3] It should be noted that in our work we assumed the formation of n-propyl phenol. According to the scheme proposed more recently by Ipatieff for alkylation and polymerization, it is to be assumed that isopropyl phenol rather than normal propyl phenol was the actual product.

Anal. 88–91°. Fraction: Calcd. for $(C_3H_7)_2O$: C, 70.5; H, 13.8. Found: C, 70.7; H, 13.7; d_0^{20}, 0.746; n_D^{20}, 1.3829.

Anal. 188–192°. Fraction: Calcd. for $C_6H_5OC_3H_7$: C, 79.4; H, 8.9. Found: C, 79.3; H, 8.9; d_0^{20}, 0.9619; n_D^{20}, 1.5011.

According to these data, the first fraction may be considered dipropyl ether, the second fraction phenyl propyl ether. The fourth fraction contained, in addition to ethers, hydrocarbons which were difficult to separate by distillation. Therefore, it was decided to separate the hydrocarbons from the ethers by decomposing the ethers by passage over alumina. In actual practice phenyl propyl ether when passed over alumina gives propylene and phenol, and the propyl ether of propyl phenol ($C_3H—C_6H_4—OC_3H_7$) which was present in the reaction products also gave propylene and propyl phenol on decomposition over alumina. The hydrocarbons present in the fourth fraction did not undergo any change and could be separated in pure state since the phenols had been extracted by treatment with alkali.

Fraction 4 was passed over alumina twice, and after treatment with alkali 70 g. of oil remained which distilled at 140–260°. This oil was a mixture of saturated and unsaturated hydrocarbons which decolorized potassium permanganate solution; there was also a very small amount of material containing oxygen. The unsaturated hydrocarbons were removed from the oil by 96% sulphuric acid followed by 7% fuming sulphuric acid, about two-thirds of the total fraction passing into solution. The remaining oil distilled at 160–210°, had a petroleum odor, did not decolorize a solution of potassium permanganate, and did not react with nitrating mixture.

Calcd. for C_nH_{2n}: C, 85.7; H, 14.3. Found: C, 85.5; H, 14.5; d_0^{20}, 0.798; n_D^{20}, 1.4352.

Without doubt, these data indicate the presence of a mixture of naphthenic hydrocarbons formed by the polymerization of propylene under elevated pressure and temperature, which are similar to the products formed by the polymerization of ethylene and isobutylene.

The investigation of the phenols (870 g.) separated from the phenolate solution was made as follows: The separated oil was dried with sodium sulphate and distilled, almost all the material coming over below 240°. Seventy per cent of this product was unchanged phenol; the remainder was a thick oil which distilled under reduced pressure, and yielded a fraction boiling at 224–232°. This last-mentioned fraction solidified in a freezing mixture to a faintly colored crystalline mass. Analysis of this crystalline material gave the following values:

Calcd. for $C_9H_{12}O$: C, 79.4; H, 8.9. Found: C, 79.1; H, 9.1; d_0^{20}, 1.012; n_D^{20}, 1.5228.

Methylation of this fraction with dimethyl sulphate gave a methyl ether boiling at 210–218°. Fusion with alkali gave salicylic acid. These data established without doubt the presence of o-propyl phenol, the wide range in boiling point being explained by the presence of isomers.

Thus, by the action of alcohols on phenols in the presence of alumina the alkylation of phenol takes place with the formation of alkyl substituted phenols, ethers of the alkyl substituted phenols forming in the interim. The reaction also has other complications. As a matter of fact, alcohols and phenols may give simple or mixed ethers under these conditions and, in addition, the aliphatic alcohol may produce olefin under the influence of alumina, and this olefin may polymerize into unsaturated and naphthenic hydrocarbons under the influence of high pressure and temperature.

ALKYLATION OF PHENOLS BY PHOSPHORIC ACID

The alkylation of phenol by amylene in the presence of sulphuric acid was first carried out by Königs.[1] Since that time the reaction has not been further investigated due to the fact that sulphuric acid was considered an unsatisfactory catalyst since it complicated the process due to its high reactivity, sulphonating the benzene nucleus and forming tarry products. It was found that alumina was not a suitable catalyst for the alkylation of phenols. Therefore, it was necessary to find another catalyst for use in the alkylation process, a catalyst which would not promote side reactions. In view of the ability of olefins to form esters with phosphoric acid which readily decompose to form polymers it was to be expected that phosphoric acid would serve as catalyst for the alkylation of other hydrocarbons by olefins, as well as certain other types of organic compounds, for example phenols. As previously shown, phosphoric acid is able to effect the alkylation of certain hydrocarbons, but it serves equally well as a catalyst in the alkylation of various types of phenols by olefins and terpenes. No experimental data regarding this reaction were to be found in the literature at the time this investigation was being made [1] with the exception of one or two patents from which no general conclusions could be drawn. Ipatieff, Pines, and Komarewsky carried out a series of experiments on the alkylation of various phenols at ordinary and at superatmospheric pressure, and the results indicated that this reaction may have a broad application in alkylation processes, excellent yields of alkylated products being obtained.

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[1] Königs, Ber., *23*, 3145 (1890).

The reaction proceeded at 100–160° at ordinary pressure. Gaseous olefins were passed into the phenol to which a small amount of phosphoric acid had been added. In case the olefin was a liquid, it was slowly added to the mixture of phenol and phosphoric acid. The reaction mixture was vigorously stirred. When the reaction was made under pressure, the mixture of olefin, phenol, and catalyst was introduced into the bomb at the beginning of the experiment.

The phosphoric acid could be recovered unchanged and could be reused in the alkylation process. It appears to be a true catalyst. The experimental data showed that one molecule of phosphoric acid is able to form thirty-six molecules of propyl phenol. At the end of the reaction, the phosphoric acid was found in the lower layer.

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[1] December, 1932; a similar study was later reported by Chichibabin, Bull. soc. chim., *2*, 497 (1935).

In the formation of ethers by reaction of phenols with olefins in the presence of phosphoric acid, the alkylated phenol was separated from the reaction product by treating with a 15% sodium hydroxide solution, the oil insoluble in sodium hydroxide being phenolic ethers. The alkali solution of phenols was treated with hydrochloric acid and the phenol separated, dried, and distilled. The alkylation reaction of phenols proceeds as follows:

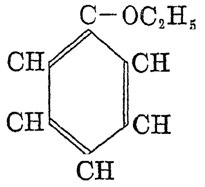
$$\text{(I)}\quad C_3H_6 + PO(OH)_3 \rightarrow PO(OH)_2O\text{—}C_3H_7$$

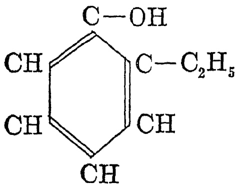
$$C_6H_5OH + PO(OH)_2O\text{—}C_3H_7 \rightarrow PO(OH)_3 + C_6H_4C_3H_7(OH)$$

$$\text{(II)}\quad C_6H_5OH + C_3H_6 + PO(OH)_3 \rightarrow C_6H_5\text{—}O\text{—}C_3H_7 + PO(OH)_3$$

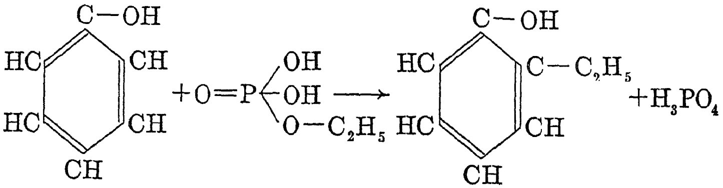
$$\text{(III)}\quad C_6H_4C_3H_7(OH) + C_3H_6 + PO(OH)_3 \rightarrow C_6H_4C_3H_7(OC_3H_7) + PO(OH)_3$$

When an alcohol or an ether is substituted for an olefin, the alkylation of phenol, similar to that caused by alumina, also takes place. In this case, the ethers *undergo isomeric transformation* into alkylated phenols. For example, in the presence of ethyl ether, phenetole is obtained as the chief product of the reaction, though it may be partially isomerized into ethyl phenol.





On the other hand, the formation of ethyl phenol may take place by direct alkylation of phenol.



The relative amounts of alkylated phenol and phenol ether depend upon the conditions of the experiment. If the reaction is

TABLE 200

ALKYLATION OF PHENOLS

SUBSTANCE ALKYLATED	ALKYLATOR	ALKYLATOR ABSORBED, G.	UPPER LAYER AFTER TREATMENT WITH NaOH, G.	PHENOL ALKYLATED, G.	B.P., ° C. OF TOTAL PRODUCT, ° C.	CHIEF PRODUCT			ANALYSIS	
						B.P., °, C.	n_D	Substance	% C	% H
Phenol	CH_3OH [a]		18	16.0	155–200	155–176		Anisole		
Phenol	C_2H_4 [a]	46.0	70	28.0	175–260	182–200	1.5052	Phenetole		
Phenol	$(C_2H_5)O$ [a]							Phenetole		
Phenol	C_3H_6 [b]	82.0		154.0	246–217	246–261	1.5126	Isopropyl phenol		
Phenol	C_3H_6 [a]		32	123.5	185–250	218–230	1.536	Isopropyl phenol	79.5	8.9
Phenol	C_4H_8 (iso) [b]	47.0			212–225	100–101 (m.p.)		Isobutyl (tri) phenol		
Phenol	Limonene [c]	75.0			175–325	318–319	1.5303	Limonyl phenol	84.2	10.0
m-Cresol	C_3H_6 [b]	41.0		108.0	225–275	225–230		Isopropyl cresol		
p-Cresol	C_3H_6 [b]	79.0	0	175.0	210–270	225–240		Isopropyl cresol		
p-Cresol	C_4H_8 [b] (iso) [b]	96.5	164	90.0	175–252	230–240	1.5171	Isobutyl ether of p-cresol	80.5 80.4	10.0 10.0
								theoret.	80.5	9 8

[a] Under superatmospheric pressure.
[b] Under ordinary pressure.
[c] The reaction of limonene with phenol was made at 70° in cyclohexane solution, 6 hours being required for the reaction.

made under elevated pressure, a large amount of phenol ethers is obtained. Phosphoric acid is an excellent catalyst for the etherification, as well as for the alkylation of phenols.

The alkylated phenols obtained were hydrogenated under pressure according to Ipatieff's method, resulting in the formation of saturated cyclic alcohols of ethereal odor. These saturated cyclic alcohols were converted into unsaturated cyclic hydrocarbons by dehydration.

Forty grams of 89% phosphoric acid and 1 mol. of phenol were used for the alkylation. The olefin was passed into the vigorously stirred mixture at 120–150° as long as it was rapidly absorbed. At the end of the reaction the upper layer was shaken with 15% sodium hydroxide solution and the insoluble oil and the alkali solution were investigated in the usual manner. Experiments made on the alkylation of various phenols by olefins, methanol, and ether are presented in Table 200.

From Table 200, it is evident that at ordinary pressure only isobutene reacts with para-cresol to form ethers as the main product, whereas propylene is converted wholly into isopropyl phenol and isopropyl cresol.

TABLE 201

ALKYLATION OF NAPHTHOLS

	ALPHA	BETA
Naphthol:		
Weight, g.	37.7	34.7
Phosphoric Acid (89%), g.	25.2	25.5
Propylene, g.	30.7	27.0
T., °C.	120	120
Time of Reaction, Hours	12.3	13
Propylene Reacted, g.	20.7	18.9
Acid Layer, g.	26.5	35.7
Upper Layer, g.	67.0	43.3
Distillation of Upper Layer, Fractions	(1) 80–300°, 3.0 g. (2) 300–340°, 49.0 g., n_D^{20}, 1.6010	(1) to 290°, 24.46 g. (2) 290–340°, 29.10 g., n_D^{23}, 1.6085

Dihydric phenols also undergo alkylation when treated with olefins in the presence of phosphoric acid at ordinary pressure. Thus, 48 g. of propylene was absorbed on passing into a vigorously stirred mixture of 70 g. of pyrocatechol and 30 g. of phosphoric acid (89%) maintained at 150°. Distillation gave following fractions: (1) up to 270° (4 g.); (2) 270–272° (17 g.); (3) 272–276° (49 g.); (4) 276–282° (18 g.); (5) 282–292° (9.5 g.). All fractions solidified and were recrystallized from petroleum ether. According to its properties the product obtained was isopropyl pyrocatechol.

Fifty grams of pyrogallol in xylene solution at 120° reacted with propylene in the presence of 89% phosphoric acid, the weight increase being 27.7 g. The product boiled at 175° (4 mm.) and solidified to a white crystalline mass. Its properties and analysis showed it to be isopropyl pyrogallol.

Alkylation experiments were also made (under pressure) with alpha- and beta-naphthol (Komarewsky), the data being summarized in Table 201.

ALKYLATION OF PARAFFIN HYDROCARBONS BY OLEFINS IN THE PRESENCE OF METALLIC HALIDES

The first experiments dealing with the action of ethylene on paraffin hydrocarbons in the presence of aluminum chloride were carried out by Ipatieff and Pines.[1] Positive results having been obtained with hexane, these experiments were repeated by Komarewsky and also studied quantitatively by Grosse, who investigated this reaction with a number of paraffin hydrocarbons.

In the chapter on "Theoretical Principles for Catalytic Reactions," an hypothesis was proposed to explain this type of alkylation in the absence of halide compounds and it was pointed out that in the presence of metallic halides the mechanism of the process is necessarily that of the Friedel and Crafts' reaction. In this section all the experimental data obtained on the alkylation of hexane, isopentane, butane, isobutane, and propane in the presence of metallic halides, particularly aluminum chloride, are discussed.

Alkylation of Hexane

When ethylene was passed into hexane (at room temperature) containing 10 parts by weight of freshly prepared and sublimed aluminum chloride, it was absorbed and there was a slight temperature rise. It was found advisable to add a small amount of hydrogen chloride during the reaction and sometimes it was advantageous to cool the mixture. The rate at which the ethylene

[1] **Riverside, June, 1932.**

was introduced was 4–5 liters per hour. After passing ethylene for 2 to 3 hours the experiment was stopped and the product was examined. In one of the experiments of Ipatieff and Komarewsky, 22.4 liters of ethylene was passed during 3½ hours through a continuously stirred mixture of 200 g. of hexane (b.p., 61–67°) and 19.5 g. of aluminum chloride. Nine liters of ethylene was absorbed and the weight of the reaction mixture increased 8 g.[1] The liquid was poured from the aluminum chloride, washed with alkali and water, distilled, and analyzed. The following results were obtained:

TABLE 202

ALKYLATION OF HEXANE BY ETHYLENE IN THE PRESENCE OF ALUMINUM CHLORIDE

FRACTION NO.	B.P., ° C.	n_D^{27}	ANALYSIS	
			% C	% H
1	70– 80	1.3800		
2	80– 90	1.3839		
3	90– 95	1.3880		
4	95–105	1.3930		
5	105–125 [a]	1.4020	84.2	15.3
6	125–140	1.4090		
7	140–190	1.4220		

[a] Specific gravity, d_{30}^{30}, 0.711.

About 15 g. of the product boiled from 80 to 220°. None of the fractions decolorized potassium permanganate solution or reacted with nitrating mixture. According to their properties and analyses these fractions must be considered to consist of paraffin hydrocarbons formed by the alkylation of hexane by ethylene. Ethyl hexane and diethyl hexane (decanes) were obtained according to these equations:

$$C_6H_{14} + C_2H_4 \rightarrow C_6H_{13}C_2H_5$$

$$C_6H_{13}C_2H_5 + C_2H_4 \rightarrow C_6H_{12}(C_2H_5)_2$$

Isopentane, likewise, undergoes the same type of alkylation. Alkylation of isopentane (b.p., 28–30°) by ethylene gave the results listed in the following table. The original isopentane was prepared by the hydrogenation of amylene.

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[1] A small amount of hexane was lost in the exit ethylene.

TABLE 203

ALKYLATION OF ISOPENTANE BY ETHYLENE IN THE PRESENCE OF ALUMINUM CHLORIDE

FRACTION NO.	B.P., °C.	n_D^{27}	ANALYSIS	
			% C	% H
1	38– 60	1.3690		
2	60– 75	1.3770		
3	75– 85	1.3830		
4	85– 95	1.3880		
5	95–105	1.3890		
6	105–120 [a]	1.3935	84.0	15.9
7	120–160	1.4055		
8	160–200	1.4190		

[a] d_4^{30} = 0.688.

When hexane and aluminum chloride were mechanically stirred 2–3 hours at 26° there was practically no change but after prolonged contacting a slight change was observed. It was necessary to raise the temperature to 60–75° in order to obtain a sufficient quantity of the reaction product for study. The chapter on "Destructive Alkylation" will deal with the decomposition of various hydrocarbons under the influence of aluminum chloride.

Ipatieff and Grosse studied quantitatively the alkylation of hexane by ethylene in the presence of aluminum chloride under ordinary and superatmospheric pressures. The apparatus used for this work was constructed in such a manner that the hexane which did not enter into the reaction was returned for further contacting with the catalyst. Precautions were taken to prevent air and moisture from entering the apparatus and to eliminate loss of reaction products. The apparatus consisted of two flasks. The first flask contained hexane and the catalyst which was vigorously stirred (mechanically) while ethylene was passed into the mixture. When a sufficient quantity of the product had accumulated, the upper layer was siphoned from the first flask into the second flask where the unchanged hexane was separated, the latter being siphoned back into the first flask and again submitted to alkylation. This cycle could be repeated indefinitely.

The hexane (147.7 g.) used in the reaction boiled at 67–68° (750 mm.); d_{30}, 0.6562; n_D^{25}, 1.3768; the ethylene was 99.6% pure. At the beginning of the experiment, 16.8 g. of aluminum chloride was present in the reaction mixture and 4.3 g. more of this catalyst was added later during the 15 hours over which the ethylene was absorbed. The temperature of the room varied between 29 and 33° during the experiment. The temperature in the reaction flask rose to 40°. Dry hydrogen chloride (a total of 25 g.) was introduced from time to time during the reaction, the size and frequency of the additions being gradually increased as the rate of ethylene absorption diminished. Altogether, 74.8 liters of ethylene was passed through the reaction mixture in 17 hours, of which 54.0 liters was absorbed (48.7 liters at 0° and 760 mm.).

Analysis of the outlet gas showed it to consist principally of ethylene which had not undergone reaction, mixed with about 5% of paraffins (perhaps propane or butane) having a paraffin index of 3.5. The liquid reaction product consisted of two layers; the lower layer contained all of the aluminum chloride and 35.0 g. of high boiling hydrocarbons formed during the reaction; the upper layer was a colorless, mobile liquid containing only traces of aluminum chloride.

From the preceding data, the following conclusions were drawn. About 75% of the hexane subjected to alkylation gave substitution products (substituted hexanes) which did not react with nitrating mixture. The properties of these fractions and their analyses indicate that they consisted of paraffin hydrocarbons. Fractions 2 to 4 were mixtures of isomeric octanes and decanes originating by the addition to hexane of one or two molecules of ethylene. There is a possibility of isomerization of the hydrocarbons initially formed and further investigations in this direction should be of assistance in the clarification of all the details of this reaction.

Tarry products were not observed in the upper layer. The presence of a small amount of low boiling hydrocarbons (b.p., 20–40°) was due to the decomposition of the hydrocarbons under the influence of aluminum chloride. Whether these low boiling hydrocarbons were formed by decomposition of paraffins in the upper layer, or of unsaturated hydrocarbons in the lower layer, is not known definitely, and this question may be answered only by further investigations. The lower layer which contained all the aluminum chloride, on decomposition by ice water, yielded a high boiling oil of unsaturated character as evidenced by its energetic reaction with both potassium permanganate solution and nitrating mixture. Obviously, the character of these hydrocarbons is similar to that of the hydrocarbons appearing in the lower layer during

TABLE 204

ALKYLATION OF HEXANE BY ETHYLENE IN THE PRESENCE OF ALUMINUM CHLORIDE

Weight Balance

Before Reaction:		*After Reaction:*	
Hexane	147.7 g.	Upper Layer	158.0 g.
Aluminum Chloride	25.1	Lower Layer	60.5
Ethylene	61.3	Loss	15.6
Total	234.1 g.	Total	234.1 g.

Properties of Upper Layer Formed in the Alkylation of Hexane by Ethylene at 29 to 40° C. in the Presence of Aluminum Chloride

FRACTION NO.	B.P., °C. @ 750 MM.	B.P., °C. CORRECTED TO 760 MM.	WEIGHT, G.	% BY WT. OF TOTAL	n_D^{20}	d_4 AT °C.	ANALYSIS		CALCULATED	
							% C	% H	% C	% H
0	20– 45		9.0	6.3						
1	45– 85		49.2	31.1	1.3784	0.6583/26	81.4	16.1	C_8H_{18}	
2	82–125		25.6	16.2	1.3955	0.6943/33	83.7	15.7	84.1	15.9
3	125–170		25.6	16.2	1.4132	0.7278/26	83.7	15.3	$C_{10}H_{22}$	
4	170–235/3 mm.		24.5	15.5	1.4300	0.7600/27	84.7	15.2	84.4	15.6
5	92–116	237–275	7.5	4.7	1.4436	0.7871/28	85.0	14.7		
6	116–140/3 mm.	275–304	4.7	3.0	1.4506	0.8146/29	85.2	14.0	$C_{24}H_{50}$	
7	140–180/3 mm.	304–353	3.9	2.5	1.4588	0.8032/28	85.0	14.5	85.3	14.7
8	Above 180/3 mm.		2.5	1.6						
Total			153.4	97.1						
Loss			4.6	2.9						

the polymerization of ethylene in the presence of aluminum chloride.

Present data indicate that the action of ethylene upon hexane and upon other paraffin hydrocarbons consists of two reactions: (1) the alkylation of paraffins by olefins, and (2) the polymerization of ethylene itself. In the case of hexane and ethylene, it may be seen that the first reaction is predominant.

Alkylation of Hexane under Pressure

In general, experiments on the alkylation of hexane by ethylene under superatmospheric pressure gave the same results as those at ordinary pressure. The only difference noted was that the reaction velocity and the yield of alkylation products under superatmospheric were greater than those obtained at ordinary pressure, which is to be expected.

Two experiments (Nos. 3 and 4) were made on the alkylation of hexane in a rotating bomb at 25–30°. The hexane used in Expt. 3 boiled at 63.8–64.5°; d_4^{25}, 0.6582; n_D^{20}, 1.3784. That used in Expt. 4 boiled at 65.1–67.3°; d_4^{25}, 0.6603; n_D^{20}, 1.3794.

TABLE 205

ALKYLATION OF HEXANE BY ETHYLENE UNDER PRESSURE IN THE PRESENCE OF ALUMINUM CHLORIDE

Weight Balance

BEFORE REACTION					AFTER REACTION			
Expt. No.	Hexane, G.	$AlCl_3$, G.	Ethylene Absorbed, G.	Total, G.	Upper Layer, G.	Lower Layer, G.	Loss, G.	Total, G.
3	141.7	28.6	112.7	283.0	228.7	53.8	0.5	283.0
4	149.2	30.4	100.2	279.8	221.5	58.3	0.0	279.8

The hexane and aluminum chloride were placed in the bomb in a glass tube (or liner) fitted with a capillary, and ethylene was added up to a pressure of 15 atmospheres. When the pressure had decreased to 2–4 atmospheres due to absorption, ethylene was again added in sufficient amount to raise the pressure to 15 atmospheres. Repressuring with ethylene was repeated eight times after which the experiment was discontinued, since the pressure then decreased only slowly. The gas was slowly released from the bomb and passed through two receivers, the first at 0°, the second at −78°. Very small amounts of liquid condensed in both receivers. The non-condensable gas collected in a gasometer totaled 2650 cc. in Expt. 3, and 600 cc. in Expt. 4. The gas from both experiments was combined and analyzed. It contained 94–95% of ethylene and 5% of paraffin hydrocarbons, paraffin index 4.5. The upper layers from the two experiments were combined, washed, dried, distilled, and analyzed. The data obtained are summarized in the following table.

TABLE 206

PROPERTIES OF THE UPPER LAYER FORMED IN THE ALKYLATION OF HEXANE BY ETHYLENE UNDER PRESSURE IN THE PRESENCE OF ALUMINUM CHLORIDE

Fraction No.	B.P., °C. @ Mm.	Hg	B.P., °C. @ 760 Mm.	Weight, G.	n_D^{20}	d^{20}	Analyses			
							Found		Calculated	
							% C	% H	% C	% H
Charge				440.4						
1	25– 50	750		8.8	1.3589	0.6550				
2	50– 75	750		150.2	1.3766	0.6604	83.8	16.5	C_8H_{18}	
3	75–100	750		21.7	1.3857	0.6785	83.3	16.1		
4	100–125	750		36.3	1.3962	0.7032	84.0	16.0	84.1	15.9
5	125–150	750		24.1	1.4058	0.7198	84.4	15.8	$C_{10}H_{22}$	
6	150–175	750		37.4	1.4147	0.7375	84.3	15.4	84.4	15.6
Residue	>175	750		153.1						
Total				431.6						
Losses (greater part gas)				8.8						
DISTILLATION UNDER VACUUM OF RESIDUE FROM ABOVE DISTILLATION										
Charge				150.8						
1	90–100	40	178–191	6.17	1.4230					
2	100–125	40	191–220	47.82	1.4270	0.7628	84.9	15.1		
3	125–150	40	220–249	24.11	1.4337	0.7755	84.5	15.1		
4	95–125	5	249–275	26.25	1.4405	0.7889	84.9	14.9	$C_{24}H_{50}$	
5	125–150	5	275–305	18.92	1.4481	0.8055	85.1	14.6	85.3	14.7
6	150–175	5	305–336	12.84	1.4547					
7	175–200	5	336–366	7.90	1.4599	0.8304	85.2	14.3		
8	200–225	5	366–396	6.15	1.4659					
Residue	Above 225	5	>396	0.5						
Total				150.66						

Of the above fractions only fraction 7 from the vacuum distillation reacted with nitrating mixture.

Comparing the data obtained by the alkylation of hexane under superatmospheric pressure with those obtained at ordinary pressure, it is seen that the reaction under these two conditions differs only in that there is a larger amount of high boiling paraffin hydrocarbons formed under pressure. Unsaturated hydrocarbons are also present in the lower layer. The ratio of the number of molecules of ethylene absorbed to the number of molecules of paraffin hydrocarbons reacting was 1.28 and 1.08 for Expts. 1 and 2 conducted at ordinary pressure. The ratios in Expts. 3 and 4 conducted under pressure were 2.45 and 2.07. That is, twice as many molecules of ethylene reacted with hexane under the pressure used as at ordinary pressure, other conditions being the same.

Alkylation of Isobutane and Butane

The alkylation of gaseous paraffins was carried out under the same conditions as those described in the case of liquid paraffins. A known weight of hydrocarbon was liquefied in a glass tube, and this liquid together with the catalyst was placed in a rotating bomb. The reaction was run at room temperature and ethylene was added repeatedly until it was no longer absorbed. At the end of the reaction the resulting gas was collected as described above, the bomb being heated in warm water in order to remove all the gas from the reaction mixture.

Alkylation of Isobutane.—The isobutane used for the experiments was 97.7% pure. Ethylene was charged into the bomb eleven times up to 15 atmospheres pressure.

TABLE 207

ALKYLATION OF ISOBUTANE BY ETHYLENE UNDER 15 ATMOSPHERES PRESSURE IN THE PRESENCE OF ALUMINUM CHLORIDE

Weight Balance

Before Reaction:		*After Reaction:*	
Isobutane	62.3	Upper Layer	142.0 g.
Aluminum Chloride	22.4	Lower Layer	31.8
Ethylene	95.6	Non-Condensable Gas (6100 cc.)	4.9
Total	180.3 g.	Loss	1.6
		Total	180.3 g.

The gas released from the bomb at the end of the experiment was almost pure ethylene (97%). The molecular ratio of ethylene to isobutane entering the reaction was 3. Distillation and analysis of the upper layer gave the data shown in Table 208.

From these data, it is apparent that the upper layer consisted principally of paraffins together with very small amounts of unsaturated hydrocarbons.

Alkylation of Butane.—The normal butane used for the experiment contained 95% of the n-butane and 5% of isobutane, pen-

TABLE 208

PROPERTIES OF THE UPPER LAYER FORMED BY ALKYLATION OF ISOBUTANE BY ETHYLENE UNDER 15 ATMOSPHERES PRESSURE IN THE PRESENCE OF ALUMINUM CHLORIDE

FRACTION No.	B.P., °C. @ 760 MM.	WEIGHT, G.	% YIELD	n_D^{20}	d^{20}	ANALYSIS			
						Found		Calculated	
						% C	% H	% C	% H
1	25– 50	7.4	5.48	1.3624	0.6398	83.3	16.5	C_6H_{14}	
2	50– 70	11.5	8.52	1.3720	0.6540	83.9	16.0	83.6	16.4
3	70–100	24.3	18.00	1.3853	0.6789	83.9	16.0	C_8H_{18}	
4	100–125	24.6	18.22	1.3992	0.7039	84.2	15.7	84.1	15.9
5	125–160	13.3	9.85	1.4086	0.7224	84.4	15.6	$C_{10}H_{21}$	
6	160–185	13.0	9.63	1.4178	0.7417	84.4	15.4	84.4	15.6
7	185–200	13.6	10.08	1.4244	0.7543	84.6	15.2		
Residue	Above 200	25.0	18.5						
Total		132.7	98.28						
Losses		2.0	1.7						

No fraction reacted with nitrating mixture.

tanes, and other hydrocarbons. The first experiment with this butane indicated that only isobutane and isopentane reacted with ethylene and that the n-butane remained unchanged. This unchanged butane was subjected to alkylation by ethylene in the presence of a mixture of aluminum chloride (17.86 g.) and aluminum bromide (8.60 g.), but without the addition of hydrogen chloride as a promoter. Ethylene was added eleven times. The amount of n-butane entering into the reaction was 25 g., that of ethylene, 43.7 g.

TABLE 209

ALKYLATION OF n-BUTANE BY ETHYLENE UNDER 15 ATMOSPHERES PRESSURE IN THE PRESENCE OF A MIXTURE OF ALUMINUM CHLORIDE AND BROMIDE

Weight Balance

Before Reaction:		*After Reaction:*	
n-Butane	56.24 g.	Upper Layer	64.00 g.
Aluminum Chloride	17.86	Lower Layer	26.46
Aluminum Bromide	8.60	Butane in Gas	31.20
Ethylene	55.00	Ethylene in Gas	11.50
		Loss	5.00
Total	138.00 g.	Total	138.00 g.

TABLE 209 (*Continued*)

ALKYLATION OF n-BUTANE BY ETHYLENE UNDER 15 ATMOSPHERES PRESSURE IN THE PRESENCE OF A MIXTURE OF ALUMINUM CHLORIDE AND BROMIDE

Distillation of the Upper Layer

FRACTION No.	B.P.,° C.	WEIGHT OF FRACTION, G.
Charge		49.65
1	45– 75	7.05
2	75–100	4.47
3	100–125	5.77
4	125–150	4.00
5	Above 150	25.80
Total		47.09
Losses		2.56

Analysis of the upper layer showed that it consisted of paraffinic hydrocarbons.

A very small amount (about 1 g.) of an oil containing unsaturated hydrocarbons was obtained by treating the lower layer with ice water. The preceding experiments show definitely that n-butane is alkylated by ethylene in the presence of a mixture of aluminum chloride and aluminum bromide without the addition of hydrogen chloride.

Alkylation of Propane

Propane was not alkylated by ethylene in the presence of aluminum chloride and aluminum bromide under the conditions indicated above.

Alkylation of Isobutane by Ethylene in the Presence of Zirconium Chloride

Experiments had shown that zirconium chloride is a considerably less active catalyst than aluminum chloride, but, nevertheless, it appears to be sufficiently useful to deserve serious consideration. The principal advantage in using zirconium chloride is the possibility of working at high temperatures. At ordinary temperature, zirconium chloride does not act catalytically, its catalytic effect becoming apparent only at 100°. The conditions under which the alkylation of isobutane by ethylene in the presence of zirconium chloride occurred were similar to those employed in the case of aluminum chloride except for the temperature, which was 100° with zirconium chloride.

TABLE 210

ALKYLATION OF ISOBUTANE BY ETHYLENE AT 100° C. UNDER 15 ATMOSPHERES PRESSURE IN THE PRESENCE OF ZIRCONIUM CHLORIDE

Weight Balance

Before Reaction:	
Zirconium Chloride	13.37 g.
Isobutane	41.48
Ethylene	34.00
Total	88.85 g.

After Reaction:	
First Receiver (0° C.)	2.76 g.
Second Receiver (–78°)	25.83
Third Receiver (–78°)	0.04
Liquid outside the Glass	2.38
Upper Layer	32.78
Lower Layer	24.16
Total	87.95 g.
Unchanged Isobutane	22.97 g.
Unchanged Ethylene in the Outlet Gases	1.68 g.

Distillation and Analysis of the Upper Layer

FRACTION No.	B.P., °C.	@ MM. Hg	WEIGHT, G.	n_D^{20}
Charge			20.50	
1	25– 50	760	1.19	1.3581
2	50– 75	760	5.09	1.3748
3	75–100	760	2.42	1.3878
4	100–125	760	4.29	
Residue	125	760	7.32	
Total			20.31	
Loss			0.19	
5[a]	125–150	760	0.92	1.4099
6	150–175	760	3.29	1.4174
7	175–200	760	0.90	1.4300
8	100–125	6	0.56	1.4368
9	125–150	6	0.24	1.4429
10	150–175	6	0.14	1.4499
11	175–200	6	0.15	1.4550
Residue	Above 200	3	0.47	1.4720
Total			6.67	
Loss			0.56	

[a] The distillation charge was 7.23 g. of residue from the preceding distillation.

It is apparent from the above table that about 50% of the isobutane was alkylated. Calculation indicates that one molecule of zirconium chloride brought about the alkylation of about six molecules of isobutane with twenty molecules of ethylene. The reaction product differed in physical appearance from that obtained with aluminum chloride. The product consisted of a colorless mobile liquid together with a dark mass of pasty consistency.

The upper layer contained only traces of zirconium chloride, distilled up to 200°, and did not react with nitrating mixture or with potassium permanganate solution. Properties and analyses indicated the material to be paraffins formed by the addition of one, two, or three molecules of ethylene to isobutane (fractions 2, 3, 4, and 6). These fractions comprised about 70% of all the hydrocarbons obtained. After removal of the upper hydrocarbon layer, the thick, dark mass remaining in the glass tube and containing all the zirconium chloride was reused as catalyst in another experiment. For this experiment 38 g. of isobutane and 32 g. of ethylene were subjected to a pressure of 35–45 atmospheres at 100°, the alkylation reaction continuing for 34 hours. At the end of the reaction, only 3.7 g. of isobutane and 17 g. of ethylene remained unchanged.

None of the fractions reacted with nitrating mixture. The dark pasty mass of the lower layer which contained all the zirconium chloride was decomposed with water to yield a small amount of a light yellow oil and a transparent solution of zirconium oxychloride.

THE ALKYLATION OF PARAFFINS WITH OLEFINS IN THE PRESENCE OF BORON FLUORIDE[1]

At first we showed that boron fluoride has no effect on paraffins, at least up to 50° C., in marked contrast to aluminum chloride. The following two experiments show this to be true:

(1) Isooctane, 100 g. of pure 2, 2, 4-trimethylpentane (b.p., 99.3°/760 mm.; n_D^{25}, 1.3893) was heated with 10 g. BF_3, 2.0 g. H_2O, and 5.0 g. Ni-powder at 50° C. for 3.0 hours. The reaction product was fractionally distilled; all fractions went over at 99° C., and had the same index of refraction (n_D^{25}, 1.3891–1.3893) and were stable towards nitrating mixture. Under the same conditions, $AlCl_3$ in the presence of HCl will completely convert this paraffin into a mixture of paraffins boiling from −10° to over 300° C.

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[1] Ipatieff and Grosse, J. Am. Chem. Soc., *57*, 1616 (1935).

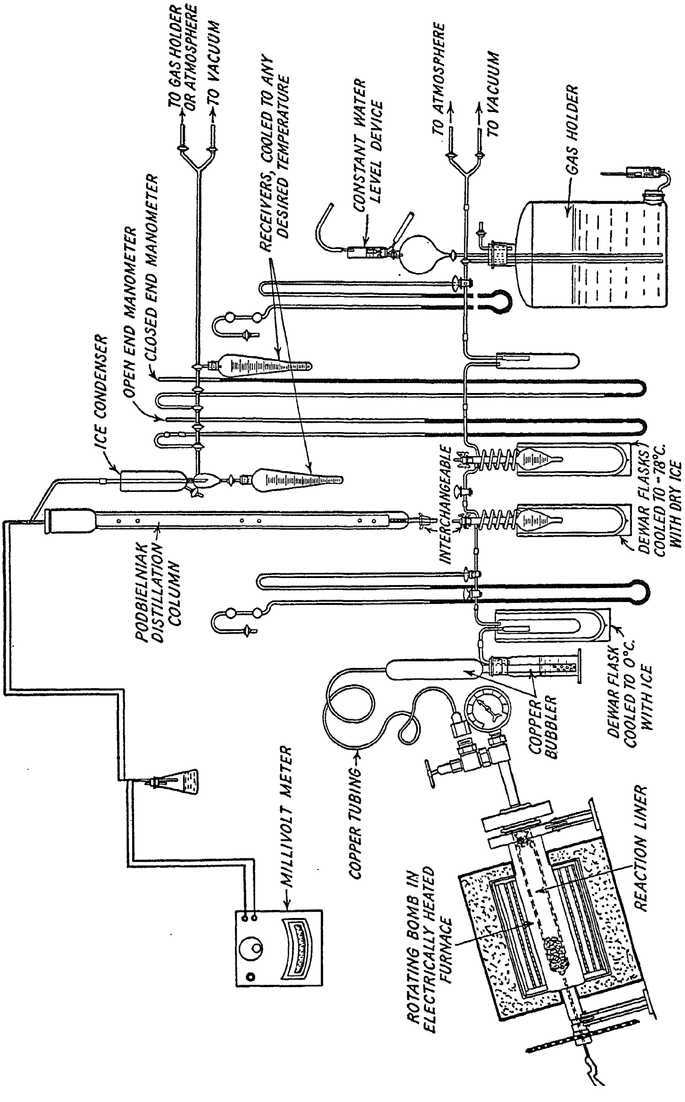
TO GAS HOLDER OR ATMOSPHERE
TO VACUUM
RECEIVERS, COOLED TO ANY DESIRED TEMPERATURE
OPEN END MANOMETER
CLOSED END MANOMETER
ICE CONDENSER
PODBIELNIAK DISTILLATION COLUMN
MILLIVOLT METER
CONSTANT WATER LEVEL DEVICE
TO ATMOSPHERE
TO VACUUM
GAS HOLDER
INTERCHANGEABLE
DEWAR FLASKS COOLED TO -78°C. WITH DRY ICE
DEWAR FLASK COOLED TO 0°C. WITH ICE
COPPER BUBBLER
COPPER TUBING
ROTATING BOMB IN ELECTRICALLY HEATED FURNACE
REACTION LINER

FIG. 50

(2) Isobutane (60 g.) was left in contact with 20 g. BF_3, 2.0 g. H_2O, and 5.0 g. Ni-powder at 50–55° C. for 24 hours. Less than 1% of paraffins boiling below and above butanes was formed and the isobutane recovered was over 98% pure.

Experimental Part

The Alkylation of Paraffins with Olefins.—The alkylation of paraffins takes place at temperatures as high as about 200° C., although it is preferably conducted at room temperature, i.e., 10–30°. Slight pressures (from 5–20 atms.) are preferably used.

As catalyst, a mixture of boron fluoride gas, finely divided metallic nickel, and small quantities of water was used. Boron fluoride alone will not effect the alkylation. The addition of metal and water are necessary. The water can be substituted by anhydrous hydrogen fluoride.

The following paragraphs will describe the alkylation of (1) isobutane with ethylene, (2) isobutane with isobutylene, (3) isopentane with ethylene, and (4) 2, 2, 4-trimethylpentane with ethylene.

Experimental Procedure.—The reaction was generally carried out in high pressure Ipatieff rotating autoclaves. Special liners were inserted into the autoclaves, glass being used in many cases when both boron fluoride and water were present. In the hydrogen fluoride experiments, Ni-liners were employed.

After the reaction, the high pressure release valve of the autoclave was connected to a high vacuum apparatus (Fig. 50) for collecting and separating the different products obtained.

The gaseous reagents such as ethylene or boron fluoride, were weighed in small dur-aluminum autoclaves (the HF in copper), and the quantity used established by difference in weight. Sometimes gaseous reagents like butane were condensed in the bomb liner, cooled to −78° (dry ice), quickly weighed, and inserted into the reaction bomb.

All the *hydrocarbons* used were 97% pure or better. The boron fluoride was purified by condensation and fractionation and stored in dur-aluminum autoclaves. The anhydrous hydrogen fluoride was prepared from dry KHF_2 and purified by redistillation, discarding the first and last fractions.

(1) *Alkylation of Isobutane with Ethylene.*—In the following table the quantities of reagents, conditions, and results of six experiments are given.

TABLE 211

Experiment No.	1	2	3	4	5	6
Isobutane, g.						
Charged	160	90	90	90	90	220
Recovered	136	2	2	1	2	40
Reacted	24	88	88	89	88	180
Ethylene, g.						
Charged	81	130	115	110	90	104
Recovered	20	0.2	0.4	1.5	5	0.1
Reacted	61	130	115	109	85	104
BF_3 Used, g.	2	8	8	14	14	30
Ni Used, g.	5.0	5.0	5.0	10.0	10.0	5.0
H_2O Used, g.	0.50	2.0	2.0	4.0	4.0	25 g. HF
Reaction Liner	Pyrex glass	Pyrex glass	Pyrex glass	Pyrex glass	Pyrex glass	Nickel
Time of Reaction, Hours	32	28	26	21	22	40
Temperature, ° C.	20–25	20–30	20–30	20–25	20–25	20–25
$n_D^{20°}$ of Total Reaction Prod.	1.4188	1.4126	1.4064	1.3998	1.3984	1.3819
Gasoline Content of Prod. 437° F. End Point, %	37	60	82	85	> 90	97
Ratio of Reacted C_2H_4 to Reacted i-C_4H_{10}, by Weight	2.5 : 1	1.5 : 1	1.3 : 1	1.2 : 1	0.97 : 1	0.58 : 1
Ratio of Reacted C_2H_4 to Reacted i-C_4H_{10}, Molecular	5.9 : 1	3.1 : 1	2.7 : 1	2.5 : 1	2.0 : 1	1.2 : 1

The reaction was effected in a rotating autoclave (30 r.p.m.) of 800 cc. capacity containing isobutane and the catalyst. The ethylene was introduced up to a pressure of 20 kg./cm.^{2}, and as the pressure dropped, fresh ethylene was added. The rate of absorption was fairly rapid, the pressure drop amounting to about 10–15 kg./cm.^{2} per hour. As the data of the table show, both gases can be made to react practically to completion. It is remarkable to see a paraffin react thus at room temperature.

An increase in the ratio of BF_3 to available paraffin increases the rate of alkylation (compare Expts. 4 and 5 with Expt. 1). The nature of the product naturally depends on the number of molecules of ethylene absorbed by a molecule of isobutane. In Expt. 1 where this ratio is high (5.9 : 1) the gasoline content of the product is low, and the boiling range extends up to 400°, whereas in Expts. 5 and 6, this ratio is below unity, and over 90% of the product represents gasoline boiling below 225°.

A matter of interest is the chemical nature of the reaction product. It consists, after removing the gaseous BF_3, principally of a water-white mobile liquid together with a small amount of a semi-solid mixture of compounds containing boron fluoride and nickel salts of boro-fluoric acids, combined with organic substances, and representing the real catalyst.

The water-white liquid was washed with water, dilute NaOH, and water (3 times), and dried over $CaCl_2$. In Expts. 3, 4, and 5 it was stable to the $KMnO_4$ test,[1] and gave no reaction (in some cases a slight coloration) with nitrating mixture, indicating the absence of any appreciable quantities of unsaturated and aromatic hydrocarbons.

Further information on the product is presented in Table 212 (Expts. 3, 4, and 5).

The chemical analysis, molecular weight determinations, indices of refraction, densities, and chemical tests (see Table 212) consistently prove that alkylation of isobutane with ethylene has taken place, and that paraffins have formed from isobutane.

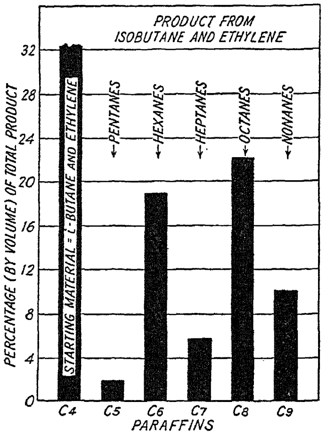

Fig. 51

Only the high boiling fractions, representing less than 5% of the product, contain unsaturated hydrocarbons. In other words the product is quite different from the straight polymerization of ethylene which gives olefins.

An important fact is noticed in evaluating the Podbielniak distillation curve, namely that the quantity of even C-number paraffins is much larger than odd C-number paraffins. This is shown in Fig. 51 where the column heights represent the amounts of pentanes, hexanes, etc., in per cent by volume of the total product.[2] The separation can be regarded only as a very rough one, even using a Podbielniak column, and decreasing rapidly in accuracy with increase in molecular weight; however, it is sufficiently accurate, below the nonane range, to indicate the pre-

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[1] The test consists in adding 2–3 drops of a 4% $KMnO_4$ solution to a solution of 2–3 drops of the substance in 2–4 cc. ethyl alcohol (96–100%); olefins rapidly decolorize the solution.

[2] The boiling ranges of paraffins were taken as follows: pentanes 5–45°, hexanes 45–75°, heptanes 75–100°, octanes 100–125°, and nonanes 125–150°.

TABLE 212

PRODUCT FROM ALKYLATION OF ISOBUTANE WITH ETHYLENE

FRACTION No.	B.P., °C. @ 760 MM.	VOL., CC.	WEIGHT, G.	COLOR	n_D^{25}	NITRATING MIXTURE TEST	ANALYSIS			MOLECULAR WEIGHT	REMARKS
							% C	% H	Total		
0	Below 0	35.1	21.80								Gas was isobutane
1	0– 45	7.6	4.76	W.W.	1.3535 @ 15						
2	45– 68	55.0	35.77	W.W.	1.3700	Stable	83.61	16.18	99.79	90	
							83.61	16.38		86	Theoretical for hexane
2A	68– 75	39.0	25.98	W.W.	1.3780	Stable					
3	75–100	25.2	17.08	W.W.	1.3870						
4	100–114	50.3	34.80	W.W.	1.3925	Stable	84.16	15.95	100.11	120	
							84.11	15.89		114	Theoretical for octane
4A	114–125	47.7	33.30	W.W.	1.3970	Stable					
5	125–150	45.0	32.01	W.W.	1.4032						
6	150–175	54.3	39.33	W.W.	1.4110						
7	175–200	43.0	31.98	W.W.	1.4187						
8	200–208	15.3	11.46	W.W.	1.4221	Stable					
Botts.	> 208	64.5	50.70	Yel.	1.4400						
Total			339.								

ponderance of hexanes and octanes over pentanes and heptanes.[1] This is to be expected, according to our alkylation equations.

It is probable that splitting of paraffins in the presence of BF_3 takes place, if it takes place at all, only *at the moment of formation,* since it has been shown that BF_3 is without action on paraffins under our experimental condition.

(2) *Alkylation of Isobutane with Isobutylene.*—This experiment was made in a rotating bomb at 25°. In one experiment 90 g. of isobutane, in the presence of 12 g. BF_3, 5.0 g. Ni-powder, and 2.0 g. H_2O (in a glass liner) reacted with about 85 g. isobutylene, which was added in small portions during a period of 20 hours. After the reaction 20 g. isobutane was recovered. After separating the BF_3 the water-white reaction product was distilled and the fractions obtained had the properties tabulated below:

TABLE 213

PRODUCT FROM ALKYLATION ISOBUTANE WITH ISOBUTYLENE

FRACTION No.	B.P., ° C.	VOL., Cc.	WEIGHT, G.	COLOR	n_D^{25}	$KMnO_4$ TEST	NITRATING MIXTURE	REMARKS
0	−10– 0	$\backsimeq$11	$\backsimeq$7	W.W.				Isobutane
1	22– 77	5.0	$\backsimeq$3.3	W.W.	1.3662	Abs. stable		
2	77– 95	2.6	1.75	W.W.	1.3837	Abs. stable		
3	95–125	30.3	20.9	W.W.	1.3943	Abs. stable	Stable	Octanes; b.p., 98–125°; d_4^{20}, 0.699
4	125–150	5.1	3.55	W.W.	1.4027		Stable	
5	150–175	5.6	4.1	W.W.	1.4122		Stable	
6	175–200	9.6	7.1	W.W.	1.4194	Abs. stable	Stable	Dodecanes; b.p., 185–220°
7	200–225	6.0	4.5	W.W.	1.4276	Abs. stable	Stable	
8 8a	225–250	5.3	4.1	W.W.	1.4392		Violet coloration; slight reaction	
9	250–275	5.6	4.4	Slightly yellow	1.4452		Partly soluble in nitrating mixture	
Botts.	>275	9.6	7.5	Yellow orange	1.4612			
Total		95	68					

Fraction #3: Found: C, 84.2; H, 15.8; Mol. Wt., 120.
Calcd. for C_8H_{18}: C, 84.1; H, 15.9; Mol. Wt., 114.
Fraction #8: Found: C, 84.7; H, 15.3; Mol. Wt., 191.
Calcd for $C_{13}H_{28}$: C, 84.7; H, 15.3; Mol. Wt., 184.
Combined Fractions #6 and #7: n_D^{25}, 1.4228; d_4^{25}, 0.755.

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[1] Small quantities of the odd C-number paraffins might be due to small quantities of isopentane present as an impurity in the original butane.

Here again we have a clear-cut alkylation of isobutane to higher molecular weight paraffins; only in the highest boiling fractions are small quantities of olefins found.

Disregarding the extreme ease of polymerization of isobutane with BF_3, H_2SO_4, H_3PO_4, and many other catalysts, the alkylation reaction proceeds smoothly and isobutylene is able to butylate isobutane at room temperature.

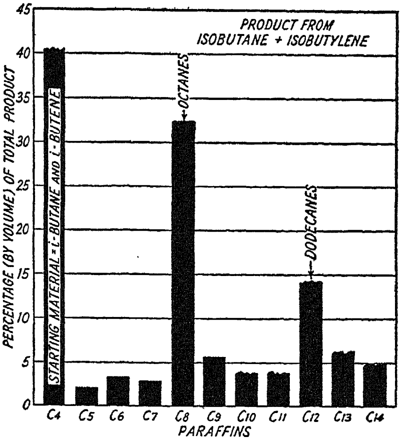

Fig. 52

The products of the reaction are mostly octanes and dodecanes (Fig. 52); the octanes form 32% of the total product. These facts support the formulation of the alkylation reaction as given above.

(3) *Alkylation of Isopentane with Ethylene.*—Isopentane was alkylated with ethylene at 25° and 150°. In an experiment at 150°, 75 g. isopentane was reacted with ethylene for 22 hours in the presence of 15 g. BF_3, 7.5 g. HF and 5.0 g. Ni-powder, at a maximum pressure of 50 atms.

About 40% of the isopentane was alkylated; the rest was recovered. The water-white mixture of paraffins obtained was fractionated with the results shown in Table 214.

(4) *Alkylation of 2, 2, 4-Trimethylpentane with Ethylene.*—This paraffin is alkylated much less readily than isobutane. Preliminary experiments show that 5–10% of the paraffin was alkylated at 25° during 40 hours with BF_3, Ni, H_2O as catalyst. At the same time polymerization of ethylene to high boiling unsaturated hydrocarbons takes place. However, paraffins are present in fractions of the product boiling below 250°, for instance, fraction 150–200°, stable to nitrating mixture, n_D^{20}, 1.4198, gave the folling values:

Anal. Calcd. for $C_{12}H_{26}$: C, 84.6; H, 15.4; mol. wt., 170. Found: C, 84.6; H, 15.4; mol. wt., 172.

(5) *The Chemistry of the Boron Fluoride Catalyst.*—The study of the chemistry of the catalyst is only in the beginning. In most

TABLE 214

Fraction No.	B.P., °C. @ 740 Mm.	Volume, Cc.	Color	n_D^{20}	Nitrating Test	Analysis			Remarks
						% C	% H	Molecular Weight	
1	25– 35	14.0	W.W.	1.3576					Isopentane
2	55– 75	14.2	W.W.	1.3723	Stable				
3	75–100	12.5	W.W.	1.3878	Stable	83.88	16.12	99	
						83.89	16.12	100	Theoretical for heptane
4	100–125	12.6	W.W.	1.4000	Stable	84.20	15.80	116	
						84.11	15.89	114	Theoretical for octane
5	125–150	8.2	W.W.	1.4138	Stable				
6	150–175	7.0	W.W.	1.4246	Stable				
Botts.	>175	31.5	Slightly yellow	1.4889	Some reaction				
Total		100.0							

The presence of even C-number paraffins indicates that some destructive alkylation has taken place.

experiments, a large portion of the boron fluoride can be recovered as such. Part of the boron fluoride reacts with a very small fraction (about 2%) of the olefin hydrocarbons, water (or hydrogen fluoride) and metallic nickel forming a complex, fuming with BF_3. This complex ranges in consistency from a liquid to a solid mass. In Expt. 4, Table 212, the complex was a heavy dark green-brown liquid (d^{20}, 1.44; vol., 22 cc.). In Expt. 6 it was a solid mass. Water decomposes these complexes and produces an oily layer of highly unsaturated hydrocarbons and a water solution of nickel salts of hydroborofluoric acids containing also some organic substances; in some cases, as for instance in Expt. 6, the reaction with water is violent, and takes place with a hissing sound similar to the quenching of iron. The catalyst is also active in the presence of sulphur.

Further investigations necessary to elucidate the exact nature of the catalyst are planned for the future.

Conclusions

It will be noted that all paraffins alkylated so far with the catalyst described contain tertiary carbon atoms. Attempts to alkylate n-paraffins, for instance, n-pentane, propane, and methane with BF_3 catalysts so far have not been successful. n-Paraffins, perhaps with the exception of ethane and methane, can be alkylated in the presence of aluminum, zirconium, and other metal halides.

ALKYLATION OF NAPHTHENES

Alkylation of Cyclohexane at Ordinary Pressure

The first experiments[1] on the alkylation of cyclohexane at ordinary pressure were negative, but methylcyclohexane and methylisopropylcyclohexane reacted with ethylene at room temperature to give hydrocarbons of saturated character. Since, from a strictly theoretical point of view, there is no evidence to contradict the possibility of alkylating cyclohexane itself, a series of experiments was made to try to find conditions under which this reaction would take place. The following reaction conditions were studied.

Ethylene was passed into cyclohexane at 70–80° after first adding 10% by weight of aluminum chloride followed by a subsequent 5% addition. The reaction was continued for several hours during which time a small amount of hydrogen chloride was passed through the mixture. Under these conditions a 20% weight increase of the cyclohexane was obtained, and also a 50% yield of an alkylated product of saturated character boiling at 90–120° at ordinary pressure with a small residue distilling up to 150° at 7 mm. This process was repeated several times. The time of the reaction was 20 hours; temperature, 70–85°; pressure, atmospheric.

The product obtained from the upper layers of all the experiments was combined, distilled, and analyzed.

All fractions were of saturated character (no reaction with nitrating mixture) and, according to their analyses, were naphthenes. The fractions boiling up to 200° contained alkylated cyclohexanes which could have been formed according to the following equations:

$$C_6H_{12} + C_2H_4 \rightarrow C_6H_{11}C_2H_5$$

$$C_6H_{12} + 2C_2H_4 \rightarrow C_6H_{10}(C_2H_5)_2$$

That is, ethylcyclohexane and diethylcyclohexane should be obtained.

In view of the experiments of Grignard and Stratford[2] which

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[1] Ipatieff and Komarewsky, Riverside (1932).

[2] Grignard and Stratford, Compt. rend., *178*, 2149 (1924).

TABLE 215

PROPERTIES OF UPPER LAYER OBTAINED BY ALKYLATING CYCLOHEXANE BY ETHYLENE AT 70–85° C. AND ORDINARY PRESSURE IN THE PRESENCE OF ALUMINUM CHLORIDE

Fraction No.	B.P., ° C.	n_D^{24}	d_4^{30}	Analysis			
				Found		Calculated	
				% C	% H	% C	% H
1	90–100	1.4224	0.7640				
2	100–110	1.4224	0.7630			C_nH_{2n}	
3	110–120	1.4225	0.7640			85.6	14.4
4	120–126	1.4232	0.7690	85.4	14.3		
5	126–130	1.4232	0.7650	85.6	14.4		
6	130–140	1.4263	0.7690	85.6	14.4		
7	140–150	1.4265	0.7759				
8	150–160	1.4300	0.7820				
9	160–170	1.4325	0.7807				
10	170–180	1.4360	0.7942	85.5	14.4		
10a	180–185	1.4340	0.7722				
11	185–195	1.4390	0.8004				
12	195–203	1.4435	0.8099	86.1	14.0		
13	203–208	1.4480	0.8190	85.9	13.9		
14	208–212	1.4520	0.8278	86.2	13.8		
15	212–216	1.4540	0.8333			$C_{12}H_{22}$	
16	216–221	1.4565	0.8380	86.3	13.6	86.7	13.3
17	221–235	1.4590	0.8424				
18	69–120/7 mm.	1.4630					
19	120–150/7 mm.	1.4860					

indicated that substituted naphthenes are readily isomerized in the presence of aluminum chloride, fractions 4, 5, and 6 were thoroughly investigated in order to identify their constituents.

In order to determine whether some of these hydrocarbons possessed six-membered cycloparaffin rings they were converted by dehydrogenation into the corresponding aromatic hydrocarbons by the method of Zelinsky, passing the naphthenes through palladium-impregnated asbestos at 300–330°. The fifth fraction was passed through the palladium catalyst four times, hydrogen being evolved and a hydrocarbon obtained which boiled at 130–140°; n_D^{24}, 1.4625. This hydrocarbon was treated with 20% oleum and found to contain 58% of aromatic hydrocarbons. The composition of the hydrocarbon remaining after treatment with 20% fuming sulphuric acid indicated a pure naphthene; n_D^{24}, 1.4270.

Anal. Found: C, 85.3%; H, 14.3%. When this hydrocarbon was subjected to repeated dehydrogenation, hydrogen separated again and a hydrocarbon was obtained with n_D^{24}, 1.4572.

In order to assure ourselves that the correct procedure had been followed in these dehydrogenation experiments, a blank experiment was made on a hydrocarbon obtained in the alkylation of hexane by ethylene. When this hydrocarbon (b.p., 105–128°; n_D^{17}, 1.4060) was passed through the palladium catalyst under the conditions previously described, no liberation of hydrogen was observed, neither was there any change in its refractive index (1.4062), or in its carbon-hydrogen content.

Anal. Hydrocarbon before passage through palladium catalyst: C, 84.2; H, 15.3. Hydrocarbon after passage through palladium catalyst: C, 84.3; H, 15.3.

Evidently, these experiments indicate that the alkyl-substituted products of cyclohexane contain a six-membered ring. As final proof of the structure of the alkylated cyclohexane the aromatic hydrocarbon obtained by dehydrogenation of the fraction boiling at 126–130° (fraction 5) was oxidized. This oxidation was accomplished by a mixture of chromic and hydrochloric acids and also by potassium permanganate solution. In both cases, isophthalic acid was obtained. Thus, in the fraction boiling at 126–130° the isomerization product, dimethylcyclohexane, was present and not ethylcyclohexane.

$$C_6H_{11}C_2H_5 \rightarrow C_6H_{10}(CH_3)_2$$

An experiment on the action of aluminum chloride upon pure ethylcyclohexane at 150° under pressure in Ipatieff's rotating bomb showed that such isomerization actually takes place. The reaction product distilled at 127–145° and on dehydrogenation an aromatic hydrocarbon was formed which reacted with bromine to give a tetrabromide melting at 244°. When oxidized it formed isophthalic acid. These data, therefore, also indicate that ethylcyclohexane isomerizes to dimethylcyclohexane.

The fractions boiling above 200° had a lower hydrogen content than naphthenes. Fraction 16 in its properties and analysis closely approached the dicyclic hydrocarbon $C_{12}H_{22}$, which could be formed by the condensation of two molecules of cyclohexane with the liberation of two hydrogen atoms.[1]

$$+ \qquad H_2 + C_{12}H_{22}$$

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[1] In all probability the hydrocarbon $C_{12}H_{22}$ (b.p., 216–221°) is an isomerization product of dicyclohexyl and dimethyldicyclopentyl. Ipatieff and Komarewsky, J. Am. Chem. Soc., *56*, 1926 (1934).

It is evident that when cyclohexane is heated with aluminum chloride a considerable amount of dicyclohexyl is formed.

Alkylation of Cyclohexane under Pressure in the Presence of Aluminum Chloride

Experiments on the alkylation of cyclohexane under pressure were made by Ipatieff and Grosse. Cyclohexane (110.3 g.) (b.p., 80.5°; n_D^{20}, 1.4268) and 10.2 g. of aluminum chloride were placed in a rotating bomb and ethylene added up to a pressure of 20 atmospheres. During 18 hours at 24° the pressure decreased to 7 atmospheres. Ethylene was added twice, and a total of 17.7 g. was absorbed. The reaction product (113 g.), after washing and drying was distilled into the following fractions:

TABLE 216

Alkylation of Cyclohexane by Ethylene under Pressure at 24° in the Presence of Aluminum Chloride

Fraction No.	B.P., °C.	Weight of Fraction, G.	n_D^{15}	d_4^{24}
1	70– 79	27.8	1.4270	
2	79– 81	61.9	1.4269	
3	81–150	9.2	1.4267	0.7680
4	150–250	4.6	1.4322	
5	250–270	1.9	1.4481	
6	Above 270	4.2	1.4481	
Total		109.5		

None of the fractions reacted with potassium permanganate solution or with nitrating mixture and according to their properties, they may be considered as naphthenes.

Further experiments on the alkylation of cyclohexane under pressure were made in order to determine the influence of hydrogen chloride. When an attempt was made to alkylate cyclohexane by ethylene under pressure at ordinary temperature without the addition of hydrogen chloride no alkylation occurred, the only reaction being the polymerization of ethylene. In these experiments ethylene was introduced 6 times up to 20 atmospheres pressure into a bomb containing cyclohexane and aluminum chloride. A 120-hour run gave the following results:

TABLE 217

ATTEMPTED ALKYLATION OF CYCLOHEXANE BY ETHYLENE UNDER PRESSURE AT ROOM TEMPERATURE IN THE PRESENCE OF ALUMINUM CHLORIDE

(Hydrogen Chloride Absent)

Weight Balance

Before Reaction:	
Aluminum Chloride	42.14 g.
Cyclohexane	396.13
Ethylene (absorbed)	44.7
Total	482.97 g.

After Reaction:	
Condensed Gas (cyclohexane)	4.2 g.
Upper Layer	418.7
Lower Layer	42.14
Aluminum Chloride + Hydrocarbons	13.0
Total	478.04 g.
Losses	4.93 g.

Distillation and Properties of the Upper Layer (400 G.)

FRACTION No.	B.P., °C. @ 760 MM.	WEIGHT, G.	d_4^{20}	n_D^{20}	M.P., °C.	REACTION WITH Potassium Permanganate	REACTION WITH Nitrating Mixture
1	47– 80	14.3	0.7738	1.4230	+1.0	None	None
2	80	160.5	0.7767	1.4265	+8.5	None	None
3	80	177.1	0.7767	1.4269	+8.5	None	None
4	80– 88	2.7		1.4232	Liquid	None	None
5	88–236	6.1	0.7714	1.4234	Liquid	Immediate decolorization	None
6	236	20.0	0.8512	1.4740	Liquid	Immediate decolorization	Energetic
Total		380.7					
Losses		19.3					

Fraction 5 was distilled and the portion boiling at 169–236° was analyzed; found: C, 84.90; H, 14.75. These data show that in the absence of hydrogen chloride there was little or no alkylation and that polymerization was almost the exclusive reaction.

Alkylation of Cyclohexane by Ethylene under Pressure in the Presence of Aluminum Chloride and Hydrogen Chloride

The alkylation of cyclohexane by ethylene in the presence of aluminum chloride and hydrogen chloride under pressure gives entirely different results. Hydrogen chloride up to 5 atmospheres pressure [1] was introduced into a rotating bomb containing cyclohexane and aluminum chloride. Ethylene was then added up to 20 atmospheres pressure, addition of the latter being repeated several times. Ethylene was rapidly absorbed.

TABLE 218

ALKYLATION OF CYCLOHEXANE BY ETHYLENE UNDER 20 ATMOSPHERES PRESSURE AT ROOM TEMPERATURE IN THE PRESENCE OF ALUMINUM CHLORIDE AND HYDROGEN CHLORIDE

Weight Balance

Before Reaction:		*After Reaction:*	
Aluminum Chloride	21.54 g.	Upper Layer	157.0 g.
Cyclohexane	100.58	Lower Layer	21.5
Hydrogen Chloride	7.4	Aluminum Chloride + Hydrocarbons	30.5
Ethylene (absorbed)	81.02		
Total	210.5 g.	Total	209.0 g.
		Losses	1.5 g.

Distillation and Properties of the Upper Layer

FRACTION No.	B.P., °C. @ 755 MM.	WEIGHT, G.	d_4^{21}	n_D^{26}	M.P., °C.
1	32.0– 80	7.5	0.7357	1.4007	
2	80 – 80.5	66.5	0.7697	1.4190	–4
3	80.5–110	4.0	1.7900	1.4082	Liquid
4	110 –190	15.0		1.4178	Liquid
5 [a]	190 –262	12.0		1.4426	Liquid
6	Above 262	15.0		1.4649	Liquid

[a] Analysis. Found: C, 85.0; H, 14.4.

None of the fractions reacted with potassium permanganate solution or with nitrating mixture and according to their properties they consisted principally of naphthenes.

Alkylation of Methylcyclohexane and p-Methylisopropylcyclohexane

Together with Komarewsky, I alkylated methylcyclohexane and p-methylisopropylcyclohexane by ethylene at 25–30° under ordinary pressure in the presence of aluminum chloride and hydrogen chloride (time of reaction, 3–4 hours). In this reaction a mixture of 100 g. of methylcyclohexane (free from toluene) and

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[1] A glass tube filled with liquid hydrogen chloride was placed in Ipatieff's bomb where it was stored free from moisture and under pressure up to 60 atmospheres without damage to the bomb. The bomb was fitted with silver valves and a silver container in which the glass tube was placed. The evaporation of solid carbon dioxide under reduced pressure was utilized for liquefying the hydrogen chloride.

10 g. of aluminum chloride absorbed 7 liters of ethylene. The resulting product consisted of two layers, the upper one containing the main portion of the reaction product. After washing and drying, the upper layer (325 g.) was distilled and analyzed.

TABLE 219

Alkylation of Methylcyclohexane by Ethylene at Ordinary Temperature and Pressure in the Presence of Hydrogen Chloride

Fraction No.	B.P., ° C.	Weight, G.	d_4^{22}	n_D^{30}	Analysis	
					% C	% H
1	I.B.P.–110	45				
2	110–115	32				
3	115–120	10	0.7669	1.3985		
4	120–130	30	0.7672	1.4205	85.5	14.3
5	130–140	32	0.7716	1.4225	85.5	14.3
6	140–148	33	0.7757	1.4250		
7	148–151	15	0.7785	1.4261		
8	151–156	30	0.7811	1.4272		
9	156–161	15	0.7831	1.4290		
10	161–171	10	0.7889	1.4315	85.5	14.3
11	171–180	7	0.795	1.4342		
12	180–190	7	0.8013	1.4375		
13	190–200	6	0.8066	1.4402		
14	Above 200	50				

Only the fraction boiling above 200° reacted with nitrating mixture. From the properties and analysis, it was concluded that the product consisted of naphthenes formed by the alkylation of methylcyclohexane.

In another experiment 60 g. of p-methylisopropylcyclohexane and 6 g. of aluminum chloride absorbed about 7 liters of ethylene. The product was separated by distillation into the following fractions: (1) 165–170° (39 g.); (2) 170–180° (5 g.); (4) > 195° (1 g.). Investigation of fractions 2 and 3 showed that alkylation of substituted naphthenes by ethylene proceeds readily at room temperature.

Alkylation of Cyclohexane by Ethylene under Pressure in the Presence of Zirconium Chloride

Ipatieff and Grosse showed that the alkylation of cyclohexane by ethylene under pressure in the presence of zirconium chloride does not take place at room temperature, but requires a temperature of 100 to 150°. If hydrogen chloride is not added the reaction product differs from that obtained by the alkylation of cyclohexane in the presence of aluminum chloride and hydrogen chloride. Further experimentation should be made concerning the alkylation of cyclohexane in the presence of zirconium chloride and hydrogen chloride.

TABLE 220

ALKYLATION OF CYCLOHEXANE BY ETHYLENE UNDER PRESSURE IN THE PRESENCE OF ZIRCONIUM CHLORIDE

Weight Balance

Before Reaction:	
Cyclohexane	84.07 g.
Zirconium Chloride	24.07
Ethylene (absorbed)	52.70
Total	160.84 g.

After Reaction:	
Gas	930 cc.
Upper Layer	117.2 g.
Lower Layer (dough-like precipitate, zirconium chloride and hydrocarbons)	43.65
Total	160.85 g.

Distillation and Properties of Upper Layer

FRACTION No.	B.P., °C. @ 750 MM. Hg	WEIGHT, G.	d_4^{19}	n_D^{20}	REACTION WITH		M.P., °C.
					Potassium Permanganate, Decolorized in	Nitrating Mixture	
0	I.B.P.- 22.0	32.00					
1	20.0- 66.0	16.03	0.668	1.3767	1 minute	Weak	
2	66.0- 74.0	22.15	0.7357	1.4078	2½ "	"	−50.0
3	74.0- 77.5	30.5	0.7599	1.4186	2½ "	"	−13.0
4	77.5- 78.0	30.5	0.7670	1.4220	2 "	"	− 6.0
5	78.0- 79.5	33.5	0.7695	1.4229	3 "	"	+ 0.5
6	79.5- 80.0	37.0	0.7700	1.4229	no reaction	"	− 5.0
7	80.0-141.0	12.2	0.7261	1.4089	" "	"	Liquid
8	141.0-181.0	9.5	0.7607	1.4269	2 minute	"	"
9	181.0-330.0	16.5	0.8580	1.4768	1½ "	Strong	"
10	Above 330.0	9.5			3 "	Very strong	"

FRACTION No.	B.P., °C.	ANALYSIS	
		% C	% H
1	20- 66	83.9	15.9
2	66- 74	84.9	14.9
7	80-141	84.7	15.3

The above reaction was run at 100° for 24 hours and then for 45 hours at 150°. The maximum pressure was 33 atmospheres, the bomb being refilled with ethylene four times. No lower layer was present at the end of the reaction. The upper layer was a brown liquid containing a small amount of hydrogen chloride, and free from zirconium chloride. Analysis of the gas (930 cc.) showed that it contained 55% of ethylene, 36% of paraffins (paraffin index 3.9), 5% of propylene, and 3% of hydrogen. A repetition of the experiment at 150° gave identical results.

According to these data it was concluded that fractions 3, 4, and 5 contained cyclohexane, that fractions 2 and 3 contained paraffins and a considerable amount of methylcyclopentane, the result of isomerization, and that fraction 7 contained paraffin hydrocarbons.

ALKYLATION OF AROMATIC HYDROCARBONS BY ETHYLENE IN THE PRESENCE OF METALLIC CHLORIDES

In order to determine the influence of other metallic halides, especially chlorides, upon the alkylation of benzene by ethylene, experiments were made by Ipatieff and Grosse using chlorides of beryllium, zirconium, titanium, columbium, and tantalum as catalysts.

In the presence of these catalysts and hydrogen chloride, benzene was alkylated by ethylene. In the absence of metal halide but in the presence of hydrogen chloride alone, no alkylation of benzene was apparent, even after 30 hours under a maximum pressure of 55 atmospheres at 230°. There was almost quantitative reaction between hydrogen chloride and ethylene under these conditions, the walls of the iron bomb acting as catalyst. In all probability ethyl chloride was formed. Experiments on alkylation in the presence of metallic halides were carried out in Ipatieff's rotating bomb under the conditions previously described, the metallic halide being placed in a glass tube provided with a capillary opening at the top.

Beryllium Chloride

Alkylation of benzene by ethylene under an initial ethylene pressure of 20 atmospheres proceeded very slowly at 125°. At 200° the reaction was more rapid. The reaction continued for sixty hours. Analysis of the non-condensable gas showed that it contained 98% of ethylene and 2% of paraffins.

A yellow liquid was obtained from the upper layer (at both 125 and 200°); at the latter temperature, the yield of this liquid was 102 g.

TABLE 221

Alkylation of Benzene by Ethylene at 125° and 200° under 20 Atmospheres Pressure in the Presence of Beryllium Chloride and Hydrogen Chloride

Weight Balance (200° Expt.)

Before Reaction:		*After Reaction:*	
Benzene	145.20 g.	Gas (non-condensable)	9200 cc.
Beryllium Chloride	6.62	Condensate (at −78° C.)	2.00 g.
Hydrogen Chloride	6.00	Liquid	224.1
Ethylene (absorbed)	93.12	Precipitate ($BeCl_2$ $C_nH_{2n}HCl$)	18.21
Total	250.94 g.	Total	244.31 g.
			6.63 g.

Distillation and Properties of the Upper Layer

Fraction No.	B.P., °C. @ 752 Mm.	Weight, G.		Reaction Product
UPPER LAYER FORMED AT 125° (CHARGE 102.0 g.)				
1	80	49.5	1.4934	Benzene
2	80	11.9	1.4957	"
3	80	14.0	1.4954	"
4	80.0–139.5	5.2	1.4922	Ethylbenzene
5	139.5–140.0	8.3	1.4923	"
6	140 and above	44.0	1.4936	Higher alkylated benzenes
UPPER LAYER FORMED AT 200° (CHARGE 12.4 g.)				
1	76.0–110.0	1.5	1.4740	Benzene, Ethylbenzene
2	110.0–178.0	3.3	1.4907	Ethylbenzene, Diethylbenzene
3	178.0–204.0	3.65	1.4963	Diethylbenzene, Triethylbenzene
4	204.0–275.0	2.8	1.510	Higher alkylated benzenes
5	275.0–290.0			Higher alkylated benzenes
6	Above 290.0			Hexaethylbenzene (crystals)

None of the above fractions reacted with potassium permanganate solution. On treating the precipitate containing beryllium chloride with water, a layer of hydrocarbons composed of ethylbenzene and higher alkylated benzenes was obtained. It is evident that the alkylation of benzene by ethylene occurs quite rapidly at 200°, though no polymerization products of ethylene are obtained.

Zirconium Chloride

Alkylation of benzene by ethylene in the presence of zirconium chloride was made by Ipatieff and Grosse at 24° for 5 hours and at 50° for 24 hours, during which time one molecule of catalyst

TABLE 222

ALKYLATION OF BENZENE BY ETHYLENE UNDER PRESSURE IN THE PRESENCE OF ZIRCONIUM CHLORIDE AND HYDROGEN CHLORIDE

Weight Balance (24–50° Expt.)

Before Reaction:	
Benzene	126.38 g.
Zirconium Chloride	12.37
Ethylene (absorbed)	58.00
Hydrogen Chloride	6.00
Total	196.75 g.

After Reaction:	
Gas (non-condensable)	900 cc.
Upper Layer	169.60 g.
Lower Layer (hydrocarbon-zirconium chloride)	27.12
Total	196.72 g.

(30–100° C. Expt.)

Before Reaction:	
Lower Layer (reused) (12.37 g. Zirconium Chloride)	27.12 g.
Benzene	136.80
Hydrogen Chloride	6.00
Ethylene (absorbed)	72.30
Total	236.22 g.

After Reaction:	
Gas (non-condensable)	5600 cc.
Gas (condensed)	3.0 g.
Upper Layer	211.3
Lower Layer	21.9
Total	236.2 g.

Properties of the Upper Layer from Second Experiment

FRACTION No.	B.P., °C. @ 747 MM. Hg	WEIGHT, G.	n_D^{26}	REACTION PRODUCT
1	80	62.3	1.4889	Benzene
2	80–140	44.7	1.4915	Ethylbenzene
3	140–188	33.9	1.4934	Diethylbenzene
4	188–224	17.1	1.4969	Tri- and tetraethylbenzene
5	224–242	17.0	1.5063	Penta- and hexaethylbenzene
6[a]	Above 242	13.0	1.5370	Oil[b] and crystals of $C_6(C_2H_5)_6$, m.p., 128–129°

[a] Fraction No. 6 reacted weakly with potassium permanganate solution, the others not at all.

[b] In addition to crystals of hexaethylbenzene there was also present an oil whose composition differed from that of the alkylated benzenes:

SUBSTANCE	ANALYSIS % C	% H
Oil (mentioned above)	89.4	10.6
Calcd. for $C_6(C_2H_5)_6$	87.7	12.3
Calcd. for $C_6H_2(C_2H_5)_4$	88.3	11.7

TABLE 223

ALKYLATION OF BENZENE BY ETHYLENE UNDER PRESSURE IN THE PRESENCE OF METALLIC HALIDES TOGETHER WITH HYDROGEN CHLORIDE

FORMULA	WEIGHT, G.	BENZENE USED, G.	ETHYLENE ABSORBED, G.	T., ° C.	TIME, HRS.	TOTAL, G.	UPPER LAYER FRACTIONS	n_D	@ ° C.	LOWER LAYER, G.	REACTION PRODUCT	EHYLENE MOLECULES ABSORBED MOL. OF CATALYST
$TiCl_4$	17.13	148.81	12.5	170	28	60.8	(1) 77.5– 80.0°	1.4910	26		(1) Benzene	
							(2) 80.0–136.0				Ethylbenzene	
							(3) 136.0	1.4908	26			
							(4) 136.0–250.0				Higher alkylated benzenes	
							(5) 250.0–260.0					
$TaCl_5$	19.71	152.69	92.82	50–75		219.7	(1) 80.0°			34.70	(1) Benzene	61
							(2) 80.0–140.0	1.4900	30		(2) Ethylbenzene	
							(3) 140.0–182.0					
							(4) 182.0–188.0	1.4915	30		(4) Diethylbenzene	
							(5) 188.0–220.0					
							(6) 220.0–236.0	1.4992	30		(8) Crystal hexaethylbenzene	
							(7) 236.0–276.0					
							(8) Above 276.0	(crystals m.p., 128–129°)				
$CbCl_5$	18.20	168.16	47.20	75	48	213.0	(1) 80.0– 81.0°	1.4920	27	18.20	Benzene	25.1
							(2) 81.0– 95.0					
							(3) 95.0–139.0		27			
							(4) 139.0–140.0	1.4922			Ethylbenzene	
							(5) 140.0–184.0					
							(6) 184.0–190.0	1.4960			Diethylbenzene	
							(7) 190.0–240.0					
							(8) Above 240.0	(crystals)			Hexaethylbenzene	

caused the absorption of 40 molecules of ethylene. The lower layer containing the zirconium chloride was reused as catalyst, continuing 10 hours at 30° and 48 hours at 100°. From this experiment 5.6 liters of non-condensable gas was collected which consisted almost entirely of pure ethylene. The upper layer (194 g.) was separated from the reaction mixture and distilled.

From the data presented in Table 222, it follows that zirconium chloride is an excellent catalyst for the alkylation of benzene. After repeated use, zirconium chloride did not lose its activity. One molecule of zirconium chloride catalyzed the absorption of 90 molecules of ethylene, indicating that this catalyst exceeds aluminum chloride in catalytic activity.

The lower layer was of a paste-like consistency and contained zirconium chloride and hydrocarbons. On decomposition with water a hydrocarbon layer was separated which was distilled and analyzed. It contained benzene, ethylbenzene, higher alkylated benzenes, and crystals of hexaethylbenzene.

Chlorides of Titanium, Columbium, and Tantalum

Alkylation of benzene by ethylene in the presence of the chlorides of titanium, columbium, and tantalum also occurred under the conditions described above. The data obtained regarding their activity are presented in Table 223. The data indicate that these metallic chlorides are able to bring about the ethylation of benzene at certain temperatures, the best catalysts of the group being zirconium chloride and tantalum chloride.

CHAPTER XIII

DESTRUCTIVE ALKYLATION

As indicated in the chapter on "Theoretical Principles for Catalytic Reactions," destructive alkylation is designated as such because under the influence of a single catalyst there occurs simultaneously the splitting up of one hydrocarbon molecule and the addition of the radical thus formed to another hydrocarbon molecule which is stable under the conditions of the experiment. Thus, for example, the saturated hydrocarbon hexane (or isooctane) splits more readily under the influence of aluminum chloride than does benzene; and therefore, when subjected to the action of aluminum chloride, hexane first decomposes into ethylene and isobutane

$$C_6H_{14} \rightarrow C_2H_4 + C_4H_{10}$$

and the ethylene then reacts with the benzene molecule forming ethylbenzene.

$$C_6H_6 + C_2H_4 \rightarrow C_6H_5C_2H_5$$

The processes of splitting and alkylation proceed simultaneously, the ethylene formed *in statu nascendi* immediatey combining with the benzene. The reaction is not greatly complicated by the polymerization of the ethylene formed in the presence of aluminum chloride, and good yields of the alkylated benzene result. Our study of this type of reaction concerns hydrocarbons only; perhaps it may also be of interest to apply it to other classes of organic compounds.

In view of the fact that a decomposition of hydrocarbons occurs in destructive alkylation, it was considered necessary to investigate the action of catalysts upon all classes of hydrocarbons under conditions of alkylation. Therefore, study was made of the action of aluminum chloride upon isooctane, hexane, benzene, cyclohexane, and isobutane.

ACTION OF ALUMINUM CHLORIDE UPON ISOOCTANE (2, 2, 4-TRIMETHYLPENTANE)

These experiments were carried out by Ipatieff and Grosse using isooctane from Rohm and Haas. This substance was distilled and a narrow fraction was used in the following study. The fraction had the following properties: b.p., 97.5° (751 mm.); n_D^{20}, 1.3923; d_4^{22}, 0.6895; d_4^{9}, 0.7068.

Isooctane previously saturated with hydrogen chloride was stirred vigorously with aluminum chloride in a three-neck flask, the evolved gas being collected in a gasometer. The reaction was started at room temperature but it proceeded very slowly, and only after the temperature was increased 15° was there any liberation of gas. The course of the reaction is evident from the data presented in the following table:

TABLE 224

GAS FORMATION DURING THE ACTION OF ALUMINUM CHLORIDE UPON ISOOCTANE

Time		Flask T., °C.	Gas Formed, Cc.
Hours	Minutes		
0		31	
1		45	500
1	20	54	3,000
1	35	61	5,900
2	15	68	5,900
2	50	70	5,900
4	15	83	5,900
4	40	91	11,000

During the reaction a lower layer containing aluminum chloride formed similar to that obtained during the polymerization of ethylene by this catalyst. At the end of the reaction the upper and lower layers were separated and analyzed. The gas formed during the reaction contained 98% of isobutane and 2% of hydrogen. Distillation of the upper layer (79 g.) gave the results shown in Table 225. All fractions except the first decolorized potassium permanganate solution, but none reacted with nitrating mixture.

It is evident that about 50% of the isooctane decomposed with the formation of isobutane and possibly isobutene if no further decomposition occurred under the given experimental conditions.

TABLE 225

ACTION OF ALUMINUM CHLORIDE UPON ISOOCTANE

Weight Balance

Before Reaction:

2, 2, 4-Trimethylpentane	135.7 g.
Aluminum Chloride	22.7
Total	158.4 g.

After Reaction:

Upper Layer	92.7 g.
Lower Layer	31.3
Gas	28.6
Total	152.6 g.
Loss	5.8 g.

Properties of the Upper Layer

FRACTION No.	B.P., °C. @ 750 MM.	WEIGHT, G.	YIELD OF UPPER LAYER, %	n_D^{20}
1	35.0– 90.0	3.1	3.9	1.3692
2	90.0– 95.0	3.9	4.9	1.3884
3	95.0– 98.4	8.4	10.6	1.3914
4	98.4–100.5	17.5	22.3	1.3932
5	100.5–106.0	19.3	24.4	1.3945
6	106.0–145.0	8.2	10.4	1.4005
7	145.0–147.0	0.2		1.4103
8	Above 147.0	15.9	20.1	1.4324

If isobutene were actually formed, it follows from our experiments on the alkylation of paraffins by olefins in which it was found that reaction between isooctane and isobutene occurred that the same reaction would take place here and that dodecanes would result. According to the boiling point of the product and its other properties, as well as the data from preceding experiments, it is evident that such alkylation occurred. This assumption was confirmed by the fact that polymerization products of isobutene were absent from the upper layer and that only a very small amount (about 8 g.) of unsaturated hydrocarbons was present in the lower layer.

The action of aluminum chloride on 2, 2, 4-trimethylpentane may be termed *auto-destructive alkylation*. Some isooctane molecules split into saturated and unsaturated hydrocarbons and the unsaturated hydrocarbon molecules alkylate the undecomposed isooctane. A study of this reaction, as well as of the action of aluminum chloride upon other hydrocarbons, clarifies the understanding of cracking which takes place in the presence of aluminum chloride.

THE ACTION OF ALUMINUM CHLORIDE UPON HEXANE AT ORDINARY PRESSURE

These experiments were made by Ipatieff and Grosse on a sample of hexane [1] (b.p., 63.8–64.3° @ 745 mm.; n_D^{20}, 1.3784; d_D^{25}, 0.6582) under conditions similar to those employed with isooctane. The hexane was first saturated with hydrogen chloride.

TABLE 226

GAS FORMATION DURING THE ACTION OF ALUMINUM CHLORIDE UPON HEXANE

TIME		T., °C. (IN FLASK)	GAS FORMED, Cc.	TIME		T., °C. (IN FLASK)	GAS FORMED, Cc.
Hours	Minutes			Hours	Minutes		
0		21		18		65	1900
	30	21		19	10	63	2100
	55	21		21	50	62	2150
1	40	53	650	(discontinued for 45 hours)			
2		59	750	67		62	2150
3		62	800	68	30	62	2950
(discontinued for 15 hours)				72		62	3000

Hexane reacted much more slowly than isooctane, an insignificant lower layer being formed only after prolonged standing. Analysis of the gas showed that it consisted of paraffins (paraffin index 3–5), i.e., principally isobutane.

TABLE 227

ACTION OF ALUMINUM CHLORIDE UPON HEXANE

Weight Balance

Before Reaction:		*After Reaction:*	
Hexane (200 cc.)	131.6 g.	Upper Layer	101.4 g.
Aluminum Chloride	24.4	Lower Layer	25.7
		Gas	7.2
Total	156.0 g.	Total	134.3 g.
		Loss	21.7 g.

Distillation and Properties of the Upper Layer (95.7 G.)

FRACTION No.	B.P., °C. @ 751 MM. Hg	WEIGHT, G.	YIELD OF UPPER LAYER, %	n_D^{20}
1	29.0–50.0	3.79	4.0	1.3669
2	50.0–63.8	67.35	70.3	1.3740
3	63.8–68.0	9.56	10.0	1.3774
4	68.0	5.65	5.9	1.4031

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[1] Considering the boiling point and other physical properties it is assumed that this hexane consisted of n-hexane, 3-methylpentane, and 2-methylpentane.

None of the fractions reacted with potassium permanganate solution or nitrating mixture. The data show that the decomposition of hexane proceeds much more slowly than that of isooctane. Perhaps, in addition to the decomposition, an isomerization of hydrocarbons also takes place. In fraction 4 a very small amount of high boiling product was present. This fact indicates that alkylation by ethylene (originating by the decomposition of hexane forming butane and ethylene) proceeds only to a small extent. The lower layer contained about 1 g. of unsaturated hydrocarbons formed by the polymerization of ethylene.

Action of Aluminum Chloride upon Hexane under Pressure

In an experiment with Komarewsky a mixture of 53.8 g. of hexane (b.p., 64–66°) and 6.6 g. of aluminum chloride was saturated with hydrogen chloride and heated in Ipatieff's rotating bomb at 70° for 23 hours, the maximum pressure being 1.8 atms. The upper layer contained 54.4 g. and the lower layer contained about 1 g. of unsaturated hydrocarbon mixed with the aluminum chloride. The upper layer was washed, dried, distilled, and analyzed.

TABLE 228

Properties of Upper Layer Formed by the Action of Aluminum Chloride upon Hexane under Pressure

Fraction No.	B.P., °C. @ 755 Mm.	Weight, G.	Yield of Upper Layer, %	n_D
1	30–55	7.0	17.0	1.3650
2	55–65	21.5	54.0	1.3700
3	65–75	6.5	16.0	1.3735
4	75–96	2.0	5.0	1.3835
5	96	1.0		

None of the fractions reacted with potassium permanganate solution or with nitrating mixture. Analysis of the gas (1 liter) from the bomb showed that it was a mixture of propane and isobutane. These results are in agreement with those obtained by the action of aluminum chloride upon hexane at ordinary pressure and lead to the same conclusions, namely, that to a certain extent, hexane undergoes auto-destructive alkylation and that isomerization also takes place.

ACTION OF ALUMINUM CHLORIDE ON BENZENE [1]

The numerous published references [2] on the action of aluminum chloride on benzene show quite different results on account of the use of different conditions in the experiments. Therefore, it was decided to study this reaction under a definite set of conditions.

In a closed autoclave, in the absence of air and in the presence of dry hydrogen chloride, the action of aluminum chloride on benzene at 125° gave 1.7% of ethylbenzene and 0.84% of diphenyl calculated on the benzene charged.

To compare these results properly with the results of other investigators, it is necessary to note the following:

(1) The absence of oxygen in our experiments accounts for the absence of phenols and other oxygen-containing compounds (obtained by Wertyporoch and Sagel [3] and Senff [4]). It is evident that in the experiments of these investigators the oxygen of air and water took part in the reaction.

(2) The reaction of benzene with aluminum chloride under our conditions proceeds much more rapidly.

(3) The main products of reaction are ethylbenzene and diphenyl. The formation of these two compounds makes probable the following scheme of the reaction: (a) benzene forms diphenyl, liberating hydrogen; (b) destructive hydrogenation of benzene occurs and the fragments are hydrogenated to form ethylene; (c) ethylene alkylates unchanged benzene to form ethylbenzene.

$$\text{(a)}\quad C_6H_6 + C_6H_6 \rightarrow C_6H_5—C_6H_5 + H_2$$

$$\text{(b)}\quad C_6H_6 + 3H_2 \rightarrow 3C_2H_4$$

$$\text{(c)}\quad C_6H_6 + C_2H_4 \rightarrow C_6H_5C_2H_5$$

The reaction of the first type (a) was observed by Friedel and Crafts,[5] Scholl,[6] and Scholl and Seer.[7] In the other two reactions,

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[1] Ipatieff and Komarewsky, J. Am. Chem. Soc., *56*, 1926 (1934).

[2] Fischer and Niggemann, Ber., *49*, 1475 (1916); Friedel and Crafts, Bull. soc. chim., *39*, 195, 306 (1883); Gustavson, Compt. rend., *146*, 640 (1908); Senff, Ann., *220*, 232 (1883); Wertyporoch and Sagel, Ber., *66*, 1306 (1933).

[3] Wertyporoch and Sagel, Ber., *66*, 1306 (1933).

[4] Senff, Ann., *220*, 232 (1883).

[5] Friedel and Crafts, Bull. soc. chim., *39*, 195, 306 (1883).

[6] Scholl, Ber., *43*, 1737, 2202 (1910).

[7] Scholl and Seer, Ann., *394*, 111 (1912).

(b) and (c), we observe first a decomposition (destruction) and then an alkylation.

Evidence that benzene decomposes in this manner follows: (1) the formation of ethylbenzene, and (2) the presence of unsaturated ethylene polymers in lower layer. It is suggested that reactions (b) and (c) be called destructive alkylation.

In these experiments about 100 g. of benzene (Baker C.P.) saturated with dry hydrogen chloride was placed in a glass cylinder and 10% by weight of aluminum chloride (obtained by sublimation) was added. The glass cylinder was placed in a rotating Ipatieff bomb (750 cc. volume) from which the air had been displaced by nitrogen and heated for twenty-four hours at 125°. At the end of the experiment, no gases were evolved, the whole product consisting of two layers. The upper layer was washed with water and 10% aqueous alkali, dried with calcium chloride, and distilled in a Podbielniak apparatus. The combined product from eight similar experiments was investigated. From 830 g. of benzene and 80 g. of aluminum chloride 904 g. of a two-layer product was obtained. The upper layer was 715 g., the lower layer 189 g. The upper layer gave on distillation 679 g. of unchanged benzene and 36 g. of a higher boiling product. The lower layer, after decomposition with ice, gave 35 g. of unchanged benzene, 10 g. of a higher boiling product (up to 250°), and 2 g. of unsaturated residue. From the upper layer 14 g. of a product boiling at 139–141° was isolated. Investigation showed that it was ethylbenzene, n_D^{20}, 1.4970.

Anal. Calcd. for $C_6H_5C_2H_5$: C, 90.56; H, 9.44. Found: C, 90.45; H, 9.50.

Oxidation with potassium permanganate gave pure benzoic acid melting at 120°. Bromination in the presence of aluminum bromide, according to Klages and Allendorf,[1] gave a pure tetrabromide, $C_6HBr_4C_2H_5$, m.p., 139–140°. From the higher boiling fractions it was possible to isolate by fractionation 7 g. of a product boiling at 235–250° which solidified in the condenser. Recrystallization of this product from benzene gave diphenyl, m.p., 70°.

Anal. Calcd. for $C_6H_5C_6H_5$: C, 93.50; H, 6.50. Found: C, 93.35; H, 6.63.

The formation of ethylbenzene is explained by assuming simultaneous decomposition and alkylation designated by the term "destructive alkylation."

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[1] Klages and Allendorf, Ber., *31*, 1005 (1898).

ACTION OF ALUMINUM CHLORIDE ON CYCLOHEXANE

From previous works by Aschan and others [1] it is known that cyclohexane isomerizes to methylcyclopentane in the presence of aluminum chloride.

In studying the action of aluminum chloride on cyclohexane under their experimental conditions, Ipatieff and Komarewsky observed more fundamental changes. By the action of aluminum chloride on cyclohexane in closed autoclaves in the presence of hydrogen chloride and in the absence of air at a temperature of 150° for twenty-four hours, the hydrocarbon changes fundamentally. Besides isomerization to methylcyclopentane, dehydrogenation occurs with subsequent combination of two cyclohexyl radicals to form a mixture of dimethyldicyclopentyl and dicyclohexyl. Evolution of hydrogen occurs and destructive alkylation reaction results in the production of m-dimethylcyclohexane. This experiment shows that (1) in order to combine two cyclohexyl radicals, it is not necessary to start with a mixture of cyclohexane and a halogen derivative ($C_6H_{11}Cl$) as is stated by Nenitzescu and Ionescu,[2] and (2) this reaction is not similar to that of Friedel and Crafts but a special reaction of destructive alkylation with formation of dimethylcyclohexane. The product boiling up to 80° is a mixture of methylcyclopentane and unchanged cyclohexane; 34% of the total product is a liquid boiling from 80 to 289°, from which 6.5% of dimethylcyclohexane and 12% of a hydrocarbon, $C_{12}H_{22}$, were isolated and identified. In addition, a certain amount (0.7–0.8%) of gas was evolved during the reaction.

Summarizing the results obtained, the most probable scheme of the reactions is as follows: (1) cyclohexane decomposes, giving ethylene. (2) Ethylene alkylates cyclohexane giving ethylcyclohexane, the latter isomerizing immediately to m-dimethylcyclohexane. (3) Other portions of cyclohexane dehydrogenate and two cyclohexyl radicals combine to form $C_{12}H_{22}$. (4) Destructive hydrogenation of cyclohexane produces paraffinic hydrocarbons, especially isobutane (see gas analysis).

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[1] (a) Aschan, Ann., *324*, 1 (1902); (b) Ipatieff and Grosse, in publication; (c) Nenitzescu and Cantuniari, Ber., *66*, 1097 (1933); (d) Zelinsky, Turowa, and Pollak, *ibid.*, *65*, 1171 (1932).

[2] Nenitzescu and Ionescu, Ann., *491*, 189 (1931).

(1)

(2) $C_6H_{12} + C_2H_4 \cdot$

(3) $C_6H_{12} + C_6H_{12} \rightarrow C_{12}H_{22} + H_2$

(4) $C_6H_{12} + 2H_2 \rightarrow \text{i-}C_4H_{10} + C_2H_6$

It is interesting to note that during this reaction there was no formation of a lower layer. The small increase in weight of the aluminum chloride may be explained by simple wetting of the catalyst by the reaction products.

The same method was used with cyclohexane (Eastman C.P.) as previously with benzene, the temperature being 150°. From 307 g. of cyclohexane (three experiments) and 33.3 g. of aluminum chloride, 332 g. of liquid products consisting of two layers was recovered. In addition, 2175 cc. of gas containing 61% of isobutane was evolved during the reaction. The upper layer amounted to 290 g. and the lower layer to 43 g. The upper layer was separated into two fractions: (1) 70 to 80°; (2) 80° and higher. The product boiling up to 80° was completely stable to nitrating mixture and was a mixture of methylcyclopentane and cyclohexane as evident from the boiling point 70 to 80° and refractive index n_D^{20}, 1.4150. From the second fraction, 19.9 g. of material boiling at 120–123° was isolated by repeated fractionation, n_D^{23}, 1.4215.

Anal. Calcd. for $C_6H_{10}(CH_3)_2$: C, 85.47; H, 14.53. Found: C, 85.68; H, 14.43.

This was a pure naphthenic hydrocarbon. It was dehydrogenated over palladium catalyst at 320°, according to Zelinsky and Borisoff.[1] The dehydrogenated product was soluble in fuming sulphuric acid (15% SO_3 content), had n_D^{19}, 1.4801, and gave after bromination according to Klages and Allendorf, a tetrabromide, $C_6Br_4(CH_3)_2$, m.p., 243°. This shows that the product was 1, 3-dimethylcyclohexane. From the same fraction 37.1 g. of a product boiling at 220° was isolated, n_D^{16}, 1.4675.

Anal. Calcd. for $C_{12}H_{22}$: C, 86.73; H, 13.27. Found: C, 86.48; H, 13.38.

This compound solidified when cooled in dry ice. The crystals were separated from residual liquid by filtering through a cooled filter. Crystallization from methyl alcohol gave a pure white substance melting at 46–47°.

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[1] Zelinsky and Borisov, Ber., *57*, 150 (1924).

Anal. Calcd. for $C_{12}H_{22}$: C, 86.73; H, 13.27. Found: C, 86.55; H, 13.30.

This compound corresponds to dimethyldicyclopentyl isolated by Nenitzescu and Ionescu.[1]

TABLE 229

PRODUCT FORMED BY THE ACTION OF ALUMINUM CHLORIDE UPON CYCLOHEXANE IN THE PRESENCE OF HYDROGEN CHLORIDE

Vigreux Cut No. 1 (B.P., below 90°) *224.0 Cc.*

FRACTION No.	B.P., ° C.	VOLUME, Cc.	n_D^{15}	REMARKS
1	37.0–53.0	7.5	1.3777	
2	53.0–68.5	9.4	1.4010	
3	68.5–70.0	14.6	1.4026	
4	70.0–72.0	11.3	1.4080	
5	72.0–73.5	22.5	1.4160	Did not solidify at 0° C.
6	73.5–74.0	30.5	1.4180	" " " " "
7	74.0–75.0	33.9	1.4165	n_D^{20}
8	75.0–76.0	47.3	1.4183	
9	76.0–79.0	35.6	1.4200	
10	79.0–80.0	23.4	1.4220	Solid at 0° C.
11	80.0–89.0	12.5	1.4235	
13	> 102.0	7.0	1.4275	

Vigreux Cut No. 2 (B.P., above 90°) *13.6 Cc. Charged*

FRACTION No.	B.P., ° C.	VOLUME, Cc.	n_D^{26}	REMARKS
1	76– 86	17.0	1.4170	
2	86–113	9.5	1.4192	
3	113–126	18.0	1.4230	
4	126–158	9.0	1.4303	
5	158–216	14.0	1.4507	n_D^{19}
6	216–224	22.5	1.4661	
7	224–232	20.5	1.4688	
8	232–256	9.0	1.4761	
9	256–286	11.5	1.4900	

Another portion of this product was dehydrogenated over palladium catalyst at 320°.[2] After the dehydrogenation, the refractive index of the product had increased from n_{16}, 1.4675 to n_{18}, 1.4815, and subsequent treatment by fuming sulphuric acid (15% SO_3 content) showed an aromatic content of 25%. The residue after sulphuric acid treatment could not be further dehydrogenated over palladium, and its analysis gave C, 86.78; H, 13.28. This investigation shows that 25% of the compound $C_{12}H_{22}$ is dicyclohexyl, the other 75% of this compound being dimethyldicyclopentyl, which could not be dehydrogenated over palladium.

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[1] *Loc. cit.*

[2] *Loc. cit.*

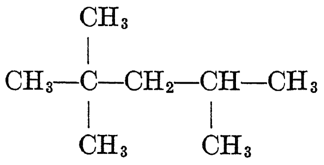
In conclusion it may be stated that the action of aluminum chloride on cyclohexane has been investigated and the formation of dimethylcyclohexane and polycyclic hydrocarbons has been observed.

The formation of dimethylcyclohexane from cyclohexane has been explained by assuming simultaneous decomposition and alkylation designated by the term "Destructive Alkylation."

Destructive Alkylation of Benzene by Paraffins

Benzene and Isooctane in the Presence of Aluminum Chloride

The first experiment on the destructive alkylation of benzene by a saturated hydrocarbon, isooctane, was carried out with Grosse at ordinary pressure. As previously indicated, the decomposition of isooctane (2, 2, 4-trimethylpentane) by the action of aluminum chloride begins at ordinary pressure, its high reactivity being attributed to its structure,



$$\begin{array}{ccccccccc} & & \mathrm{CH_3} & & & & & & \\ & & | & & & & & & \\ \mathrm{CH_3} & — & \mathrm{C} & — & \mathrm{CH_2} & — & \mathrm{CH} & — & \mathrm{CH_3} \\ & & | & & & & | & & \\ & & \mathrm{CH_3} & & & & \mathrm{CH_3} & & \end{array}$$

The reaction between benzene and isooctane was carried out in a flask with vigorous stirring in the presence of $AlCl_3$ and a small amount of dry hydrogen chloride, air having been displaced from the apparatus by dry nitrogen. The outlet gas from the reflux condenser passed through three receivers cooled with solid carbon dioxide, and then through a mercury manometer to a calibrated gas holder. The isooctane was added dropwise to the benzene. Reaction began at room temperature and during 4.5 hours the temperature increased steadily to 50°. The reaction products consisted of condensable and non-condensable gases, and upper and lower liquid layers. The non-condensable gas (800 cc.) consisted of 80% of nitrogen,[1] 6% of paraffin, and 14% of ethylene. A total of 67.57 g. of colorless condensable gas was collected in the first receiver; nothing condensed in the second and third receivers. Podbielniak analysis of the condensed gas showed that it consisted of 62.5 g. of isobutane, 4.73 g. of benzene entrained by the gas stream and traces (0.3 g.) of propane and pentane.

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[1] In the reaction flask, 800 cc. of nitrogen was displaced by isobutane, the weight of which was calculated as 2.2 g.

The upper layer was a colorless liquid; n_D^{20}, 1.4663; d_4^{20}, 0.7960. Its distillation data and properties are given in the following table:

TABLE 230

Action of Aluminum Chloride upon Mixture of Isooctane and Benzene in the Presence of Hydrogen Chloride

Weight Balance

Before Reaction:	
Aluminum Chloride	18.2 g.
Isooctane (2, 2, 4-trimethylpentane)	160.1
Benzene	127.3
Total	305.6 g.

After Reaction:	
Uncondensed Gas	2.2 g.
Condensed Gas	67.57
Upper Layer	202.5
Lower Layer	32.6
Total	304.9 g

Properties of the Upper Layer

Fraction No.	B.P., °C. @ 752 Mm.	Weight, G.	Yield, %	d_4^{22}	n_D^{20}	Paraffin Hydrocarbons, % of Upper Layer	n_D^{20} after Treatment with Fuming Sulphuric Acid
Charge	192.0						
1	71.0- 80.0	10.7		0.8198	1.4659	18.5	1.3966
2	80.0- 81.5	64.9	35	0.8270	1.4711	18.0	1.3920
3	81.5-173.0	21.0		0.7635	1.4332	45.0	1.3938
4	173.0-174.0	63.1	34	0.8644	1.4916	0.0	
5	174.0-192.0	0.2				0.0	
6	192.0-216.0	30.2		0.8751	1.4949	2.0 +	
7	216.0	2.5			1.5267	2.0 +	

Fraction 4 was the principal reaction product and it contained no paraffin hydrocarbons since it dissolved completely in fuming sulphuric acid (15% SO_3). The first three fractions contained unreacted benzene and isooctane. Fraction 6 was almost wholly aromatic.

On the basis of the experimental data it is calculated that 61 g. of benzene had reacted with 137 g. of isooctane. The product consisted of 63 g. of a fraction boiling at 173–174°, 30 g. of a fraction boiling at 192 to 216°, and 64.5 g. of isobutane.

Pure isobutane was present in the gas and the 173–174° fraction contained tertiary butylbenzene. The reaction is summarized as follows:

$$(CH_3)_3C—CH_2—CH(CH_3)_2 \rightarrow C_4H_{10} + C_4H_8$$
$$C_6H_6 + (CH_3)_2C{=}CH_2 \rightarrow C_6H_5—C(CH_3)_3$$

Proof of the structure of the aromatic hydrocarbon in the 173–174° fraction was sought by bromination and sulphonation. Bromination was carried out by adding 18 g. of bromine dropwise to 15 g. of the hydrocarbon in the presence of 1 g. of reduced iron. After the addition, the mixture was heated on a water bath for one hour. The bromide was washed with alkali and water, dried, and distilled; the yield of monobromide was about 90% of the theoretical. It distilled chiefly at 230–231°; m.p., 19°; d_4^{15}, 1.2159; n_D^{22}, 1.5281.

Anal. Calcd. for $C_{10}H_{13}Br$: Br, 37.51%. Found: Br, 36.5%.

The bromide crystallized in needles and in its other properties were similar to those of the bromide which Schramm obtained by brominating tertiary butylbenzene.

For the sulphonation of the fraction boiling at 173–174°, 16 g. of the hydrocarbon was treated with 18 cc. of 100% sulphuric acid. The solution was then diluted and neutralized by barium hydroxide solution and the barium salt of the sulphonated hydrocarbon was filtered and crystallized. Twenty-three grams of barium salt was obtained in the form of white crystalline flakes. The barium salt of the sulphonated hydrocarbon was converted into the potassium salt and fused with potassium hydroxide. The phenol which was obtained quantitatively in the form of crystalline needles melted at 98.5°. According to its properties it was identical with tertiary butyl phenol which Komarewsky obtained by alkylating phenol with isobutene in the presence of phosphoric acid.

In addition to tertiary butylbenzene which was the principal reaction product (b.p., 173–174°) there was also a large (30 g.) sixth fraction. On cooling this fraction about 8 g. of crystals separated which after recrystallization from methyl alcohol melted at 75–76°, di-para-tertiary butylbenzene. Pines and Corson had obtained the same crystals by the alkylation of benzene with isobutene in the presence of sulphuric acid and phosphoric acid. The di-para-tertiary butylbenzene obtained was about 50% of the sixth fraction, the residual liquid being presumably a mixture of the ortho- and meta-isomers.

Investigation of the lower layer showed that it contained a small quantity of unsaturated hydrocarbons formed by the polymerization of isobutene, and a considerable quantity of di-tertiary butylbenzene, as well as benzene combined with aluminum chloride. After treating the lower layer with water, about 10 g. of hydrocarbon was obtained which distilled between 80 and 335°.

Thus, by the action of isooctane upon benzene in the presence of aluminum chloride a splitting of isooctane into isobutane and isobutene takes place and almost all of this isobutene reacts with benzene to give tertiary butylbenzene and di-tertiary butylbenzene.

Alkylation of Benzene by Isooctane in the Presence of Zirconium Chloride [1]

The reaction of benzene and isooctane in the presence of zirconium chloride was made under pressure (maximum pressure, 7.5 atmospheres) in a rotating bomb, first at 50° for 1.5 hours, and later at 75° for 2 hours.

TABLE 231

INTERACTION OF ISOOCTANE AND BENZENE IN THE PRESENCE OF ZIRCONIUM CHLORIDE

Weight Balance

Before Reaction:		*After Reaction:*	
Benzene	63.0 g.	Gas	0.0 g.
2, 2, 4-Trimethylpentane	78.5	HCl (in NaOH)	4.0
Zirconium Chloride	16.7	Condensed Gas	41.6
Hydrogen Chloride	8.0	Upper Layer	82.5
		Lower Layer (hydrocarbons)	21.3
Total	166.2 g.	Zirconium Chloride	16.7
		Total	166.1 g.

Properties of the Upper Layer

FRACTION No.	B.P., °C. @ 745 MM.	WEIGHT, G.	d_4^{20}	n_D^{20}	AROMATIC HYDROCARBONS, %	n_D^{28} (AFTER TREATMENT WITH H_2SO_4 + SO_3)	ACTION OF POTASSIUM PERMANGANATE SOLUTION
1	79– 84	27.5	0.8495	1.4755	86	1.3905	None
2	84–173	9.0	0.8521	1.4755	90	1.4255	"
3	173–174	28.5	0.8666	1.4890	100		"
4	174–224	11.0	0.8732	1.4904			"
5	224–256	5.5		1.4988			Very weak
6	Above 256	2.0					

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[1] Ipatieff and Grosse, unpublished results.

The condensed gas consisted of 97% (40.5 g.) of isobutane and 3% (1.3 g.) of benzene. The upper layer, a colorless liquid, was distilled and analyzed. The data are summarized in Table 231.

The chief reaction products were tertiary butylbenzene, ditertiary butylbenzene (para isomer isolated in crystalline form) and unchanged benzene and isooctane.

The lower layer on decomposition with water gave about 17 g. of hydrocarbons which yielded analytical data corresponding to those of benzene, tertiary butylbenzene, and a hydrocarbon boiling above 235° which according to its analysis (C, 89.8%; H, 9.4%) was a polycyclic hydrocarbon formed perhaps by polymerization of isobutene or by alkylation of benzene by isobutene. In the alkylation of benzene with isooctane hydrogen may be formed as in other cases of alkylation, and it could be consumed in the reduction of unsaturated hydrocarbons, e.g., isobutene. Actually, the weight balance of the reaction indicated a somewhat larger amount of isobutane than that required by theory; 40 g. being obtained, whereas only 37.5 g. of isobutane should be present. It is evident that the destructive alkylation of benzene by isooctane in the presence of zirconium chloride gives the same general results as were obtained in the presence of aluminum chloride.

Destructive Alkylation of Benzene by Other Paraffins in the Presence of Aluminum Chloride

Experiments were made with Komarewsky on the destructive alkylation of benzene by hexane, isopentane, and butanes, using a rotating bomb containing aluminum chloride. The reaction time was 24 hours; the temperatures varied from 100 to 175°; the pressure developed during the reaction depended upon the temperature and varied from 8 to 15 atmospheres.

Hexane and Benzene.—Before adding the aluminum chloride the hydrocarbons were saturated with hydrogen chloride. The reaction (at 100°) gave the results shown in Table 232.

Analysis of the gas showed that it consisted of 3150 cc. of condensable gas and 1450 cc. of incondensable gas. The condensable gas was composed almost wholly of saturated hydrocarbons, about 71% of isobutane and 24% of propane. The uncondensable gas was 95% nitrogen.

The upper layer was washed, dried, and distilled into the following fractions: (1) up to 90 (52.7%); (2) 90 to 220° (47.3%).

TABLE 232

DESTRUCTIVE ALKYLATION OF BENZENE BY HEXANE IN THE PRESENCE OF ALUMINUM CHLORIDE AT 100°

Weight Balance

Before Reaction:		*After Reaction:*	
Benzene	50.0 g.	Gas (4600 cc.)	5.8 g.
Hexane (b.p., 65.2°)	50.0	Upper Layer	72.4
Aluminum Chloride	10.0	Lower Layer	28.2
Total	110.0 g.	Total	106.4 g.

Podbielniak Distillation of the 90 to 220° Portion of the Upper Layer

FRACTION No.	B.P., ° C.	AMOUNT, Cc.	n_D^{16}
1	79–110	13.0	1.4825
2	110–132	7.8	1.4810
3	132–138	14.0	1.4890
4	138–140	9.8	1.4900
5	140–142	22.4	1.4955
6	142–192	9.5	1.4915
7	192–210	6.0	1.4960
8	Above 210	3.0	1.5100

The second fraction (88 cc.) gave the distillation data shown in above table.

It is seen from these distillation data that about 80% boiled from 132 to 142°. By its index of refraction, and other properties, this fraction was identified as ethylbenzene. Analysis of the fraction boiling at 138–140° gave the following data:

Anal. Calcd. for $C_6H_5C_2H_5$: C, 90.6; H, 9.4. Found: C, 90.2; H, 9.8.

One and one-half grams of this fraction was oxidized with potassium permanganate to benzoic acid, m.p., 121°. Bromination of another portion of this fraction in the presence of aluminum gave the tetrabromide, $C_6HBr_4C_2H_5$, m.p., 140°. The hydrocarbon was stable to potassium permanganate solution and dissolved completely in fuming sulphuric acid.

The higher fractions (6 and 7) probably contained diethylbenzene. The hydrocarbons which separated when the lower layer was decomposed with water were chiefly aromatic (including benzene) mixed with small amounts of unsaturates.

Thus, under the conditions of the experiment hexane split into isobutane and ethylene and the latter alkylated benzene to ethylbenzene. Calculation indicated that a 60% yield of ethylbenzene was obtained, and that 30% of the hexane did not react.

Isopentane and Benzene.—Isopentane obtained by the hydrogenation of trimethylethylene was used for this reaction. The temperature was 125°; the hydrocarbon mixture was previously saturated with hydrogen chloride.

TABLE 233

Destructive Alkylation of Benzene by Isopentane in the Presence of Aluminum Chloride at 125°

Weight Balance

Before Reaction:		*After Reaction:*	
Isopentane	35.3 g.	Gas (4650 cc.)	10.3 g.
Benzene	36.0	Upper Layer	51.2
Aluminum Chloride	7.0	Lower Layer	16.5
Total	78.3 g.	Total.	78.0 g.

Podbielniak Distillation of the 90–260° Portion of the Upper Layer

Fraction No.	B.P., °C. @ 749 Mm.	Amount, Cc.	Yield, %	Analysis		
				% C	% H	
Charge	51.0 cc.					
1	80– 81	8.0	12.0			
2	81–138	5.0	12.5			
3	138–140	22.0	40.0	90.3	9.8	n_D^{14}, 1.4950
4	140–170	9.0	15.0			
5	170–225	3.0	10.0			
6	>225	3.5	7.0			

Low temperature distillation of the gas showed that it contained 22.3% of propane, 9.4% of isobutane, the residue being unchanged isopentane.

The upper layer was distilled, 25% of the product distilling between 90 and 260°. All the hydrocarbons of the upper layer were saturated hydrocarbons which did not react with potassium permanganate solution though they did react rather vigorously with nitrating mixture.

These data show that isopentane is decomposed into ethylene and propane, and that the ethylene alkylates benzene giving a considerable amount (up to 40% of the total fraction boiling from 90 to 260°) of ethylbenzene. Oxidation with potassium permanganate solution resulted in the formation of benzoic acid.

Butanes (n-Butane and Isobutane).—When heated with benzene in the presence of aluminum chloride at various temperatures

(100–175°) butane gave considerable amounts of alkylated products, as much as 50% of a fraction boiling from 90 to 230°. However, it was found that there was the same amount of butane after reaction as there was before reaction. In the meantime, it was established that benzene alone gives only 6% of alkylated products under these conditions. Up to the present time, we have not determined the reason for such an increase in destructive alkylation.

Propane also reacts with benzene in the presence of aluminum chloride producing considerable amounts of primary and secondary products.

Destructive Alkylation of Benzene by Hexane in the Presence of Phosphoric Acid [1]

In view of the fact that phosphoric acid is a catalyst for the alkylation of phenols by olefins, as well as for aromatic hydrocarbons by isobutene, it seemed interesting to test phosphoric acid as catalyst for destructive alkylation. Experiments showed that phosphoric acid acted catalytically but a higher temperature (425–450°) was required. At this temperature, when benzene was used alone with phosphoric acid, no reaction took place. Hexane begins to decompose above 450° to form small amounts of high boiling products containing a small amount of olefins (about 3%).

The reaction was made in a silver lined rotating bomb; 51.2 g. of hexane (b.p., 66.2–67.0°), 51 g. of benzene, and 10.7 g. of 100% phosphoric acid were used for the reaction. The reaction was run 24 hours at 450°. The reaction produced 4950 cc. of condensable gas and 8100 cc. of non-condensable gas. The condensable gas was a mixture of 2.5% of olefins, 96% of paraffins (paraffin index 2.9), and 1.5% of hydrogen. The non-condensable gas was a mixture of 96% of paraffins and 4% of hydrogen.

Sixty-four grams of liquid product was obtained which showed the following properties.

TABLE 234

Fraction No.	B.P., °C. @ 755 Mm.	Weight, G.	n_D^{22}	Action of $H_2SO_4 + 15\%\ SO_3$
1	Up to 90	33.2	1.4540	
2	90–140	5.7	1.4930	Dissolved completely
3	140–200	14.0	1.4930	Dissolved completely
4	200–360	8.1		

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[1] Ipatieff, Pines, and Komarewsky, J. Am. Chem. Soc., *58*, 918 (1936).

The above data indicate that alkylation of benzene took place, as does also the fact that a product was isolated from the third fraction which boiled at 138–142° and possessed the properties of ethylbenzene.

DESTRUCTIVE ALKYLATION OF CYCLOHEXANE BY HEXANE IN THE PRESENCE OF ALUMINUM CHLORIDE [1]

A study of the alkylation of cyclohexane by hexane is complicated by the fact that cyclohexane and hexane can decompose to give ethylene which can alkylate both cyclohexane and hexane.

Data obtained for the action of hexane upon cyclohexane at 175° are presented.

Hexane (60.4 g.; b.p., 65.2°), cyclohexane (60.4 g.), aluminum chloride (12 g.), and hydrogen chloride were taken for the reaction; the reaction time was 22 hours; the temperature 175°.

Gas (400 cc.) and 128.6 g. of liquid resulted from the reaction. The gas was chiefly paraffinic (paraffin index 2.3). The liquid separated from the lower layer containing aluminum chloride was washed and distilled into two fractions: (1) up to 90° (80%); and (2) 90–240° (20%). The second fraction was distilled with the following results:

TABLE 235

Fraction No.	B.P., °C. @ 756 Mm.	Amount, Cc.	n_D^{16}	Analysis			
				Found		Calculated	
				% C	% H	% C	% H
Charge	72.0 cc.						
1	79–100	10.5	1.4220				
2	100–117	12.8	1.4245				
3	117–127	11.0	1.4260				
4 [a]	127–162	11.0	1.4360	b.p., 234–235°		$C_6H_{11}—C_6H_{11}$	
5	200–234	14.5	1.4653	86.6	13.4	86.7	13.2
6	234–248	7.0	1.4675				
7	>248	4.5	1.4822				

[a] d_4^{20}, 0.857.

Distillation indicated the presence in fractions 3 and 4 of a product resulting from the alkylation of cyclohexane with ethylene. Investigation [2] showed that m-dimethylcyclohexane and not ethylcyclohexane was present due to isomerization under the influence of aluminum chloride.

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[1] Ipatieff and Komarewsky, unpublished work.

[2] Ipatieff and Komarewsky, J. Am. Chem. Soc., *56*, 1926 (1934).

The properties and analyses of fractions 5 and 6 indicated the presence (to the extent of 25%) of a product containing condensed nuclei, probably dicyclohexyl [1] boiling at 234–235°. The reaction with cyclohexane does not proceed as smoothly as does that with benzene since cyclohexane is, under the experimental conditions, less stable than benzene in the presence of aluminum chloride.

Action of Isopentane upon Cyclohexane in the Presence of Aluminum Chloride

This reaction was made at 150° and a 27% yield of saturated alkylated products was obtained. Thirty-six grams of isopentane, 35.3 g. of cyclohexane saturated with hydrogen chloride, and 7 g. of aluminum chloride were used. During 23 hours, 1350 cc. of gas and 71.3 g. of liquid product were obtained. The gas consisted principally of paraffinic hydrocarbons with a paraffin index of 5 (isopentane). Sixty-three per cent of the liquid distilled up to 90°, and 27% from 90 to 280°. The second fraction (68 cc.) was distilled with the following results:

TABLE 236

Fraction No.	B.P., °C. @ 760 Mm.	Amount, Cc.	n_D^{16}
1	78–125	29.5	1.4230
2	125–161	11.0	1.4340
3	161–244	15.5	1.4630
4	250–270	8.0	1.4792
5	Above 270	3.0	1.4990

The result was the same as with hexane; a considerable amount of dicyclohexyl was obtained simultaneously with alkylated cyclohexane.

Action of Aluminum Chloride upon a Mixture of Cyclohexane and Benzene

The preceding experiments showed that benzene decomposes slightly (about 6%) at 150–175° in the presence of aluminum chloride. Cyclohexane decomposes much more readily than benzene, setting free about 40% of products boiling between 90 and 218°.

Thus, it is to be expected that from the above combination of hydrocarbons a larger amount of alkylated products would be obtained. Fifty grams of cyclohexane, 50 g. of benzene saturated with gaseous hydrogen chloride, and 10 g. of aluminum chloride were used for the experiment; the duration of the experiment was 24 hours, the temperature 175°. Thirty atmospheres pressure of nitrogen were pumped into the bomb. As a result of the reaction, 19,025 cc. gas and 108.6 g. liquid product were obtained. Analysis of the condensable gas showed that it was made up principally of paraffinic hydrocarbons with a paraffin index of 5.

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[1] Perhaps it also contained dimethyldicyclopentyl.

The liquid product consisted of two layers.[1] The upper layer was washed and distilled into two fractions: (1) up to 90° (41%); (2) 90–260° (59%). The presence of aromatic hydrocarbons was determined in the second fraction by treatment with fuming sulphuric acid (15% oleum).

TABLE 237

Properties of Product Obtained by Action of Aluminum Chloride on Mixture of Cyclohexane and Benzene

Fraction No.	B.P., °C.	Aromatic Hydrocarbons, %
1	Up to 90	46
2	90–120	74
3	120–200	80
4	200–360	71

Fraction No.	B.P., °C.	Amount, Cc.	n_D^{14}	Analysis			
				Found		Calculated	
				% C	% H	% C	% H
1	78–116	9.8	1.4565			$C_6H_4(CH_3)_2$	
2	116–132	12.9	1.4590				
3	132–140	5.2	1.4730				
4	140–142	6.8	1.4845	90.2	9.8	90.6	9.4
5	160–228	17.9	1.4890				
6	228–252	9.9	1.5018				
7	252		1.5280				

Investigation of the products indicated that alkylation of benzene by ethylene (formed by decomposition of cyclohexane) had taken place to the extent of at least 15%, forming the products boiling between 140° and 144°.[2] Distillation of fractions 5 and 6 gave a hydrocarbon boiling at 210–215° which, according to analysis, and also its reaction with nitrating mixture, suggested the structure of cyclohexylbenzene, $C_6H_{11}C_6H_5$.

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[1] When benzene was used for destructive alkylation, two layers were always obtained, the lower layer containing aromatic hydrocarbons, as well as olefins. In the absence of benzene, the amount of lower layer was negligible.

[2] This product is a dimethylbenzene. Oxidation gave phthalic acid; bromination, a bromide melting at 255°.

This product was formed from a molecule of benzene and one of cyclohexane by the elimination of hydrogen under the influence of aluminum chloride. This reaction is similar to the action of aluminum chloride upon cyclohexane and benzene separately, reactions which result in the formation of dicyclohexyl and its isomer from the former and of diphenyl from the latter.

These reactions represent only the first steps in the study of destructive alkylation. Further investigation is necessary in order to understand the course of destructive alkylation.

APPENDIX

Numerous experiments made upon the catalytic polymerization of individual olefins [1] led to the conclusion that this process could be utilized for the polymerization of olefins in cracked gases. The two following papers [2] indicate the commercial possibilities of the catalytic polymerization of the gaseous olefins—ethylene, propylene, and the butylenes—occurring in refinery gases.[3]

POLYMERIZATION—A NEW SOURCE OF GASOLINE

A new catalytic process has been developed for the production of gasoline from the olefins in cracked gas and a plant is in commercial operation which is capable of processing 3,000,000 cubic feet of gas per day.

The commercial plant (Fig. 53) has operated continuously for 52 days producing 570,000 gallons of 81 octane gasoline from the olefins in 116,500,000 cubic feet of gas whose propylene-butylene content was 27%.

The yearly production of cracked gas in this country as a by-product of the cracking process is 300,000,000,000 cubic feet of which 50,000,000,000 cubic feet are olefins. The latter has a potential production of 1,000,000,000 gallons of polymer gasoline of 81 octane number. The total gasoline production in this country in 1934—straight-run and cracked—was 17,785,000,000 gallons of about 65 octane number.

Mild operating conditions, of 230° C. and 200 pounds per square inch, have been found satisfactory in this polymerization process. The catalyst is a hard, gray to white, granular solid, which is non-corrosive. It is not poisoned by carbon monoxide, hydrogen sulphide, mercaptans, or other constituents of refinery gases. The catalyst gradually loses its activity with continued use, but can be readily regenerated to its original activity

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[1] Ipatieff, Ind. Eng. Chem., *27*, 1067 (1935); Ipatieff and Corson, Ind. Eng. Chem., *27*, 1069 (1935); presented April 24, 1935, in New York as part of the Symposium of Gaseous Hydrocarbons before the Joint Meeting of the Petroleum and Gas Divisions.

[2] Ipatieff, Corson, and Egloff, Ind. Eng. Chem., *27*, 1077 (1935); presented April 24, 1935 in New York before the Joint Meeting of the Petroleum and Gas Divisions.

Ipatieff and Corson, Ind. Eng. Chem., *28*, 860 (1936); presented April 15, 1936 in Kansas City, Mo., before the Petroleum Division of the American Chemical Society.

[3] Pilot plant operation was carried out in Riverside. The experimental investigation of the process was made by Ipatieff, together with Corson, Skowronski, Schaad, and Kurbatov. Skowronski also studied operation on larger scale plants in East Chicago from a chemical engineering point of view.

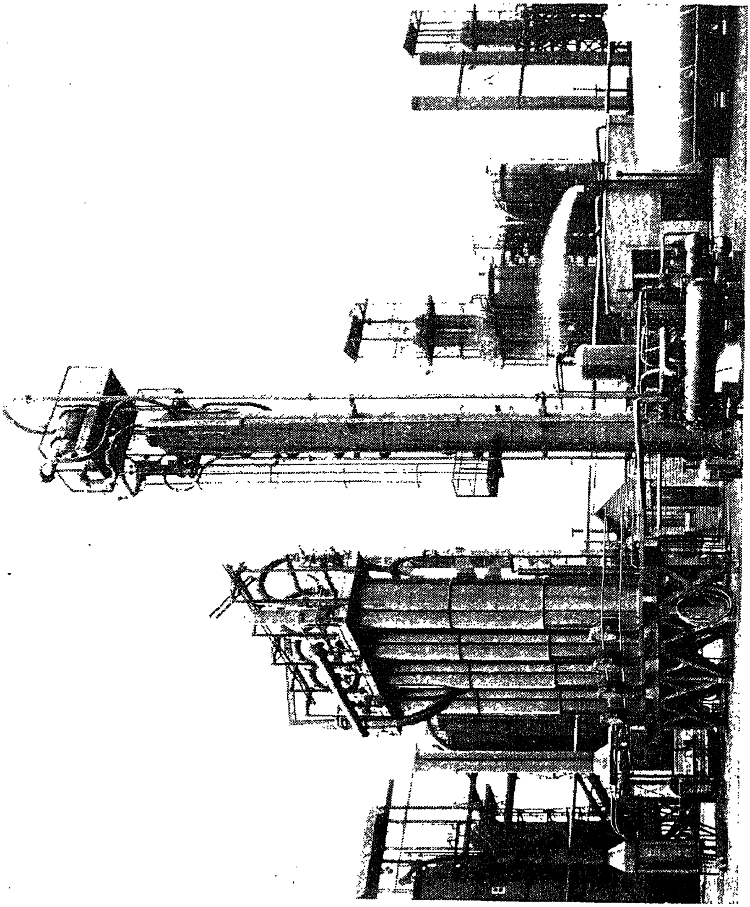

Fig. 53

with a time efficiency of over 90%. Regeneration consists in removing high polymer hydrocarbons or carbonaceous material from the catalyst by air oxidation. Regeneration has been accomplished without removing the catalyst from the polymerization towers.

Early in this work it was realized that the polymerization of the less reactive olefins is accelerated by the presence of the more active olefins.[1] For example, pure α-butylene was not polymerized by a weak catalyst under certain experimental conditions, whereas a commercial sample of butylenes (which contained 30% of isobutylene mixed with α- and β-butylenes) was polymerized by the same catalyst to the extent of 50% under identical experimental conditions.

Also, polymer liquid produced from mixtures of olefins is somewhat different than that obtained from the individual olefins due to combination of the different olefins, e.g., propylene with butylene to form heptylene.

The data reported here were obtained in a pilot plant capable of processing about four hundred cubic feet of olefin-containing gas per day. Certain of these results have also been duplicated in a larger pilot plant of 75,000 cubic feet daily capacity. A 3,000,000 cubic feet commercial plant is ready to go into operation to produce high octane gasoline from cracked gases.

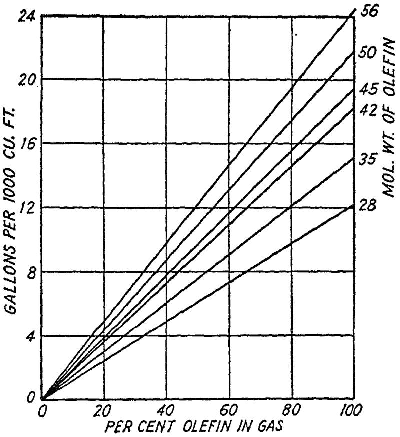

FIG. 54

The small pilot plant consisted of four vertical, electrically heated towers in series flow charged with catalyst, and a stabilizer. The plant was designed to operate at pressures up to 1,500 pounds per square inch at the temperatures employed. The gas entered the unit through a constant pressure valve, and a valve between the last catalyst tower and the stabilizer column maintained the latter at 100 pounds pressure.

The cracked gases were received in cylinders at pressures of 100 to 1,000 pounds per square inch. High percentage olefinic gases, such as "stabilizer reflux," were emptied into a charger equipped with a Jerguson gage glass and the liquid was forced into the polymerizing unit by means of nitrogen at constant pressure. Low percentage olefinic gases, such as pressure still "receiver gas," were pumped into a steam-heated, high-pressure gas holder which was connected to the polymerizing unit by means of a steam-heated pipe line. The gas being processed passed over the solid catalyst at temperatures of 204 and 232° C. and pressures of 100 and 200 pounds per square inch. The spent gas issued from the top of the stabilizer column and liquid polymer was continuously drawn off from the bottom of the column. Twenty-four hour composite samples of inlet and outlet gas were analyzed. The gas analytical values used in calculating the olefin polymerization were obtained by absorption of propylene-butylenes by 87% sulphuric acid and ethylene by bromine.

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[1] Ipatieff and Corson, Ind. Eng. Chem., *27*, 1071 (1935); Ipatieff and Schaad, unpublished work.

The theoretical yield of liquid polymer (Fig. 54) was calculated on the basis of the gravity of the liquid product and the average molecular weight of the olefins contained in the gas as calculated from Podbielniak distillation data.

The complete analysis of the gas was determined by a combination of fractional distillation and absorption methods. The gas was separated into fractions corresponding to C_1, C_2, C_3, C_4, and C_5 by low temperature Podbielniak distillation and each fraction was subsequently analyzed for olefin content by absorption.

The two methods of gas analysis, absorption and distillation-absorption, checked each other within 2–5%. For example, the propylene-butylene content of receiver gas was 17.1% according to absorption and 15.2 according to distillation-absorption.

POLYMERIZATION OF PRESSURE STILL "RECEIVER GAS" (FROM "LIQUID-VAPOR PHASE" CRACKING)

This gas was obtained in the cracking of a mixture of Mid-continent and West Texas Topped Crude, the separation of the gas from the gasoline produced being made at 75 pounds pressure. The average olefin content of the gas was 17.1% of propylene-butylenes and 7.2% of ethylene. The polymerization of this "receiver gas" was studied at temperatures of 204 and 232° C. and pressures of 100 and 200 pounds per square inch at a number of feed rates. Increase in temperature from 204 to 232° C. (with equal contact times) increased the extent of polymerization about 15%. The olefin polymerization at a given temperature and contact time was the same at 100 and 200 pounds. The polymerization of propylene-butylenes ranged from 64 to 95% and that of ethylene from 13 to 31%.

Typical analyses of the inlet and outlet gases are given in Table 238, columns 1 and 2 of which show the actual gas analysis figures, whereas the values in column 3 have been corrected for the change in gas volume due to polymerization. The values in columns 1 and 3 represent the relative volumes of the inlet and outlet gases, respectively, that is, for every hundred cubic feet of inlet gas there were eighty-two and five-tenths cubic feet of outlet gas.

It is to be noted that less than 40% of the hydrogen sulphide of the inlet gas appeared in the outlet gas. The remainder reacted during the polymerization process to form sulphur derivatives of the liquid polymers. About 90% of the sulphur content of the polymer was in the form of mercaptan sulphur.

TABLE 238

Analysis of Inlet and Outlet Gases

	In, %	Out, %	Out, % × 0.825
Hydrogen	4.3	5.2	4.3
Methane	22.2	24.9	20.6
Ethylene	6.0	7.0	5.8
Ethane	17.3	25.2	20.8
Propylene	11.2	1.8	1.5
Propane	26.8	26.3	21.7
Butylenes	4.0	0.6	0.5
Butane	5.6	6.7	5.5
Pentane	0.2	0.4	0.3
Carbon Monoxide + Nitrogen	1.6	1.5	1.2
Hydrogen Sulphide	0.8	0.4	0.3
Total	100.0	100.0	82.5

The boiling range of the polymer was raised by increase in the reaction temperature and also by increase in the contact time. For example, the A.S.T.M. 100 cc. distillation temperature at the 90% point was 11 to 22° C. higher for polymers produced at 232° C. than for polymers made at 204° C.

Run data are presented in Table 239 showing the operating conditions, the olefin content of the gas, the extent of olefin polymerization, and the liquid yields obtained by passing the cracked gas through the catalyst bed but once.

TABLE 239

Operating Conditions:			
Hours on Test	120	120	120
Gage Pressure, Lbs./Sq. In.	200	200	200
Temperature, ° C.	204	232	232
Inlet Gas Rate, Cu. Ft./Hr./Lb. of Catalyst	2.1	1.3	0.5
Olefin Content of Gas:			
Propylene and Butylenes, %	17.3	18.6	16.8
Ethylene, %	6.6	7.2	7.0
Olefin Polymerization:			
Propylene and Butylenes, %	64	79	95
Ethylene, %	13	16	31
Gallons of Liquid Polymer and of Gasoline per 1000 Cu. Ft. of Gas:			
Liquid Polymer	2.9	3.8	4.0
Gasoline (Init. B.P., 134° F.; E.P., 401° F.)	2.7	3.5	3.7

Distillation and other characteristics of the crude liquid polymer as produced are presented in Table 240.

TABLE 240

Crude Liquid Polymer

Gravity, ° A.P.I. at 60° F. (15.6° C.)	61.2
Spec. Grav. at 60° F. (15.6° C.)	0.734
Sulphur, %	0.4
Octane Number (C.F.R. Motor Method)	82
Reid Vapor Pressure at 100° F., Lbs.	8.5

100 Cc. A.S.T.M. Distillation

Per Cent Distilled Over	° F.	° C.
Init. B.P.	125	52
5	167	75
10	189	87
20	216	102
30	232	111
40	245	118
50	260	127
60	277	136
70	301	149
80	331	166
90	388	198
End Point	481	249

The crude polymer was steam-distilled and the resulting gasoline had the following properties.

TABLE 241

Polymer Gasoline

Gravity, ° A.P.I. at 60° F. (15.6° C.)	61.8
Spec. Grav. at 60° F. (15.6° C.)	0.732
Color, ° Saybolt	30
Color Stability [a]	22
Gum, Mg./100 cc. (Copper Dish)	5
Induction Period, Minutes	40
Induction Period + 0.025% Wood Distillate Inhibitor	275
Sulphur, %	0.4
Octane Number (C.F.R. Motor Method)	82
Octane Blending Value (25% in Fuel A-3; C.F.R. Motor Method)	120
Reid Vapor Pressure at 100° F., Lbs.	5.0

[a] Equivalent to two hours noon June sunlight.

TABLE 241 (*Continued*)

Polymer Gasoline

100 Cc. A.S.T.M. Distillation

Per Cent Distilled Over		
Init. B.P. . .	134	57
5. . . .	180	82
10. . . .	194	90
20. . . .	212	100
30. . . .	225	107
40. . . .	237	114
50.	248	120
60.	261	127
70.	280	138
80.	303	151
90.	337	169
End Point.	401	205

Polymerization of "Stabilizer Reflux" (from "Liquid-Vapor Phase" Cracking)

Cracked distillate is stabilized by fractionation under pressure to the desired vapor pressure and "stabilizer reflux" is the liquid condensate which is circulated through the stabilizing tower. It is a gas at atmospheric temperature and pressure. The "stabilizer reflux" whose polymerization is described below, contained 37.5% of propylene and butylenes and a trace of ethylene.

Table 242 presents gas analytical data which is complete except for hydrogen sulphide which was scrubbed out by caustic solution before distilling through the Podbielniak column.

TABLE 242

Analysis of "Stabilizer Reflux"

	Per Cent
Hydrogen.	0.1
Methane.	0.1
Ethylene.	0.6
Ethane.	3.2
Propylene.	16.6
Propane.	16.8
Isobutylene.	10.2
n-Butylenes.	10.2
Isobutane.	20.5
n-Butane.	20.0
Pentane +.	1.2
Nitrogen.	0.5

This gas was processed at 204° C. and 100 pounds pressure with three feed rates. In a number of the runs the gas was analyzed as it came out of each of the four catalyst towers and it was noted that 75% of the total polymerization took place in the first two catalyst towers and only 25% in the last two towers.

Run data on the polymerization of "stabilizer reflux" on a once-through basis are listed in Table 243.

TABLE 243

Operating Conditions:			
Hours on Test	72	72	72
Gage Pressure, Lbs./Sq. In.	100	100	100
Temperature, ° C.	204	204	204
Inlet Gas Rate, Cu. Ft./Hr./Lb. of Catalyst	4.9	3.4	2.1
Olefin Content of Gas:			
Propylene and Butylenes, %	37.5	37.5	37.5
Olefin Polymerization:			
Propylene and Butylenes, %	72	81	89
Gallons of Liquid Polymer and of Gasoline per 1000 Cu. Ft. of Gas:			
Liquid Polymer	6.0	6.9	7.2
Gasoline (Init. B.P., 150° F.; E.P., 389° F.)	5.4	6.2	6.5

Distillation and other characteristics of the crude liquid polymer are presented in Table 244.

TABLE 244

CRUDE LIQUID POLYMER

Gravity, ° A.P.I. at 60° F. (15.6° C.)	64.6
Spec. Grav. at 60° F. (15.6° C.)	0.722
Sulphur, %	0.18
Octane Number (C.F.R. Motor Method)	81
Reid Vapor Pressure at 100° F., Lbs.	11.0

100 Cc. A.S.T.M. Distillation

PER CENT DISTILLED OVER	° F.	° C.
Init. B.P.	103	39
5	153	67
10	174	79
20	194	90
30	207	97
40	217	103
50	229	109
60	248	120
70	283	139
80	328	164
90	404	207
End Point	459	237

Steam-distillation of the crude polymer yielded a gasoline with the properties shown in Table 245.

TABLE 245

POLYMER GASOLINE

Gravity, ° A.P.I. at 60° F. (15.6° C.)	62.8
Spec. Grav. at 60° F. (15.6° C.)	0.728
Color, ° Saybolt	30 +
Color Stability [a]	21
Gum, Mg./100 Cc. (Copper Dish)	4
Induction Period, Minutes	40
Induction Period + 0.025% Wood Distillate Inhibitor	275
Sulphur, %	0.16
Octane Number (C.F.R. Motor Method)	82
Octane Blending Value (25% in Fuel A-3; C.F.R. Motor Method)	121
Reid Vapor Pressure at 100° F., Lbs.	5.0

100 Cc. A.S.T.M. Distillation

PER CENT DISTILLED OVER	° F.	° C.
Init. B.P.	150	66
5	177	81
10	192	89
20	203	95
30	211	99
40	218	103
50	225	107
60	239	115
70	258	126
80	285	141
90	326	163
End Point	389	198

[a] Equivalent to 2 hours noon June sunlight.

POLYMERIZATION OF "STABILIZER GAS" (FROM "VAPOR-PHASE" CRACKING)

This gas was obtained from the top of the fractionating column used in the stabilization of gasoline produced by "vapor-phase" cracking. The gas contained 39.1% of propylene-butylenes, 3.3% of butadiene, and 20.0% of ethylene. The butadiene was determined by the maleic anhydride method.[1] For the purposes of calculation, the butadiene was included with the propylene-butylenes.

Table 246 presents gas analytical data which is complete except for hydrogen sulphide which was scrubbed out by caustic solution before distilling through the Podbielniak column. The low sulphur content of the liquid polymer (0.03%) shows that the amount of hydrogen sulphide in the gas was small.

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[1] Tropsch and Mattox, Ind. Eng. Chem., Anal. Ed., *6*, 104 (1934).

TABLE 246

ANALYSIS OF "STABILIZER GAS"

	PER CENT
Hydrogen	0.8
Methane	3.4
Ethylene	16.0
Ethane	17.8
Propylene	29.0
Propane	22.2
Isobutylene	2.9
n-Butylenes	2.0
Butadiene	3.3
Butane	2.0
Pentane +	0.2
Nitrogen	0.4
Hydrogen Sulphide	0.2

The gas was processed at 100 pounds per square inch gage pressure and at temperatures of 204 and 232° C. Depending upon the operating conditions, the polymerization of propylene-butylenes ranged from 78 to 96% and that of the ethylene from 7 to 35%. The temperatures 204 and 232° C. were practically equivalent for the polymerization of propylene and butylenes except at the shortest contact times. In the case of ethylene, the higher temperature gave 5 to 10% more polymerization at short contact times, but the two temperatures were equivalent in polymerizing effectiveness at the longer contact times. Under the experimental conditions studied, the ethylene polymerization contributed 1 to 10% of the total yield of liquid polymer.

The decrease in gas volume caused by passing through the polymerization unit averaged 39%, that is, for every hundred cubic feet of inlet gas there were 61 cubic feet of exit gas. This gas shrinkage varied from 3[illegible] to 45% under the operating conditions.

The feed rate, within the range studied, had very little effect upon the boiling point of the liquid polymer except for the end points. Contrary to the behavior of pressure still "receiver gas," the higher operating temperature produced a lower boiling product, the 50% point of polymer product made at 232° C. being about 14° C. lower than the 50% point of polymer product made at 204° C.

Typical run data are presented in Table 247 showing operating conditions, olefin content of the gas, extent of olefin polymerization, and the liquid yield on a once-through basis.

TABLE 247

Operating Conditions:			
Hours on Test	120	72	72
Gage Pressure, Lbs./Sq. In.	100	100	100
Temperature, ° C.	232	232	232
Inlet Gas Rate, Cu. Ft./Hr./Lb. of Catalyst	1.7	0.9	0.3

Olefin Content of Gas:			
Propylene and Butylenes, %	43.9	42.6	42.7
Ethylene, %	20.2	21.6	21.2
Olefin Polymerization:			
Propylene and Butylenes, %	84	94	96
Ethylene, %	8	25	32
Gallons of Liquid Polymer and of Gasoline per 1000 Cu. Ft. of Gas:			
Liquid Polymer	7.6	8.5	8.4
Gasoline (I.B.P., 142° F.; E.P., 414° F.)	6.3	7.1	7.0

Distillation and other characteristics of the crude liquid polymer are presented in Table 248.

TABLE 248

CRUDE LIQUID POLYMER

Gravity, ° A.P.I. at 60° F. (15.6° C.)	57.1
Spec. Grav. at 60° F. (15.6° C.)	0.750
Sulphur, %	0.03
Octane Number (C.F.R. Motor Method)	83
Reid Vapor Pressure at 100° F., Lbs.	9.5

100 Cc. A.S.T.M. Distillation

PER CENT DISTILLED OVER	° F.	° C.
Init. B.P.	113	45
5	177	81
10	200	93
20	228	109
30	245	118
40	267	131
50	287	142
60	320	160
70	350	177
80	395	202
90	456	236
End Point	549	287

Steam-distillation of the crude liquid polymer produced gasoline with the properties shown in Table 249.

TABLE 249

POLYMER GASOLINE

Gravity, ° A.P.I. at 60° F. (15.6° C.)	60.2
Spec. Grav. at 60° F. (15.6° C.)	0.738
Color, ° Saybolt	25
Color Stability [a]	19
Gum, Mg./100 cc. (Copper Dish)	72
Gum + 0.025% Wood Distillate Inhibitor	2
Induction Period, Minutes	55
Induction Period + 0.025% Wood Distillate Inhibitor	610

[a] Equivalent to 2 hours noon June sunlight.

Sulphur, %	0.04
Octane Number (C.F.R. Motor Method)	82
Octane Blending Value (25% in Fuel A-3, C.F.R. Motor Method)	116
Reid Vapor Pressure at 100° F., Lbs.	5.2

100 Cc. A.S.T.M. Distillation

Per Cent Distilled Over	° F.	° C.
Init. B.P.	142	61
5	178	81
10	194	90
20	216	102
30	234	112
40	251	122
50	266	130
60	284	140
70	304	151
80	324	162
90	360	182
End Point	414	212

The distillation characteristics of the crude liquid polymer are further illustrated by the following Podbielniak distillation data (see also Fig. 55).

TABLE 250

Distillation of Crude Liquid Polymer

Fraction No.	Per Cent Distilled Over	Boiling Point	
		° F.	° C.
Gas	5.2	– 54	– 12
1	4.0	54–163	12 – 73
2	3.4	163–187	73 – 86
3	1.9	187–201	86 – 94
4	5.8	201–217	94 –103
5	6.0	217–226	103 –108
6	5.9	226–244	108 –118
7	6.5	244–266	118 –130
8	2.5	266–281	130 –138.5
9	8.1	281–286	138.5–141
10	7.1	286–315	141 –157
11	6.1	315–336	157 –169
12	7.9	336–363	169 –184
13	5.7	363–399	184 –204
14	6.3	399–425	204 –218.5
15	4.1	425–451	218.5–233
16	2.0	Above 451	Above 233
Bottoms	9.8		
Loss	1.7		

POLYMERIZATION OF "STABILIZER REFLUX" (FROM "VAPOR-PHASE" CRACKING)

The average olefin content of this gas was 64.1% of propylene-butylenes, 3.0% of butadiene, and 0.8% of ethylene. For the purposes of calculation the propylene-butylene content was taken as 67.1%, i.e., the sum of the propylene-butylenes and the butadiene.

This gas was processed at 204 and 232° C. at 200 pounds per square inch gage pressure. The conversion of propylene-butylenes into liquid polymer varied from 84 to 99%, depending on the operating conditions. At the feed rates studied, the two temperatures, 204 and 232° C., were equivalent in polymerizing effectiveness.

Typical analyses of the inlet and outlet gases are presented in Table 251. Columns 1 and 2 give the actual gas analyses, whereas the values in column 3 have been corrected for the change in gas volume due to polymerization. That is, for every hundred cubic feet of inlet gas there were 25.7 cubic feet of outlet gas. In the period corresponding to these gas analyses the olefin conversion into liquid was 99%, and the yield of polymer gasoline per 1000 cubic feet of gas was 12 gallons.

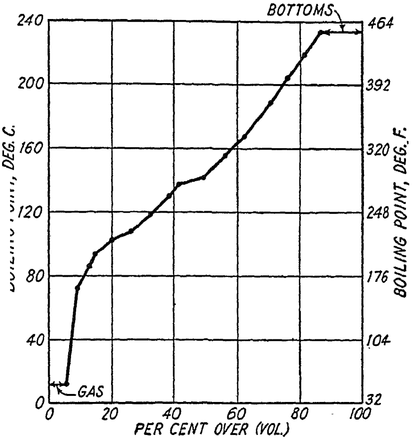

FIG. 55

TABLE 251

ANALYSES OF INLET AND OUTLET GASES

	IN, %	OUT, %	OUT % × 0.257
Propylene	45.2	3.1	0.9
Propane	30.2	89.4	22.8
Butylenes + Butadiene	19.9	2.8	0.7
Butane	4.6	4.1	1.1
Pentane +	0.1	0.6	0.2
Total	100.0	100.0	25.7

Table 252 lists data illustrative of the operating conditions, the olefin content of the gas being processed, the extent of olefin polymerization, and the liquid yield on a once-through basis. The Reid vapor pressures of the crude polymer were high, ranging from 11.6 to 14.3 pounds.

TABLE 252

Operating Conditions:			
Hours on Test	72	72	72
Gage Pressure, Lbs./Sq. In.	200	200	200
Temperature, ° C	204	204	204
Inlet Gas Rate, Cu. Ft./Hr./Lb. of Catalyst	3.7	2.4	0.8
Olefin Content of Gas:			
Propylene and Butylenes, %	70.4	69.2	69.4
Olefin Polymerization:			
Propylene and Butylenes, %	84	93	99
Gallons of Liquid Polymer and of Gasoline per 1000 Cu. Ft. of Gas:			
Liquid Polymer	12.4	14.2	15.0
Gasoline (I.B.P., 132° F.; E.P., 406° F.)	9.7	11.1	12.0

Distillation and other characteristics of the crude liquid polymer as produced are listed in Table 253.

TABLE 253

CRUDE LIQUID POLYMER

Gravity, ° A.P.I. at 60° F. (15.6° C.)	58.5
Spec. Grav. at 60° F. (15.6° C.)	0.745
Sulphur, %	0.02
Octane Number (C.F.R. Motor Method)	81
Reid Vapor Pressure at 100° F., Lbs.	14.2

100 Cc. A.S.T.M. Distillation

PER CENT DISTILLED OVER		
Init. B.P.	112	44
5	160	71
10	194	90
20	234	112
30	260	127
40	284	140
50	310	154
60	334	168
70	366	186
80	414	212
90	512	267
End Point	542	283

Steam-distillation of the crude polymer produced a polymer gasoline with the following properties.

TABLE 254

POLYMER GASOLINE

Gravity, ° A.P.I. at 60° F. (15.6° C.)	60.3
Spec. Grav. at 60° F. (15.6° C.)	0.738
Color, ° Saybolt	30 +
Color Stability [a]	23
Gum, Mg./100 Cc. (Copper Dish)	61

[a] Equivalent to 2 hours noon June sunlight.

Gum + 0.025% Wood Distillate Inhibitor	4
Induction Period, Minutes	60
Induction Period + 0.025% Wood Distillate Inhibitor (Minutes)	735
Sulphur, %	0.02
Octane Number (C.F.R. Motor Method)	82
Octane Blending Value (25% in Fuel A-3; C.F.R. Motor Method)	115
Reid Vapor Pressure at 100° F., Lbs	5.2

100 Cc. A.S.T.M. Distillation

PER CENT DISTILLED OVER	° F.	° C.
Init. B.P.	132	56
5	184	84
10	206	97
20	236	113
30	254	123
40	268	131
50	286	141
60	302	150
70	322	161
80	338	170
90	364	184
End Point	406	208

The distillation characteristics of the crude liquid polymer are further illustrated by the following Podbielniak distillation data (see also Fig. 56).

TABLE 255

DISTILLATION OF CRUDE LIQUID POLYMER

FRACTION NUMBER	% DISTILLED OVER	BOILING POINT	
		° F.	° C.
Gas	12.4	–54	– 12
1	3.8	54–181	12 – 83
2	3.5	181–187	83 – 86
3	3.8	187–192	86 – 89
4	3.5	192–203	89 – 95
5	4.8	203–212	95 –100
6	3.2	212–226	100 –108
7	3.8	226–246	108 –119
8	4.1	246–266	119 –130
9	5.7	266–288	130 –142
10	5.2	288–306	142 –152
11	6.0	306–315	152 –157
12	5.5	315–329	157 –165
13	4.7	329–338	165 –170
14	5.4	338–360	170 –182
15	5.8	360–394	182 –201
16	5.1	394–424	201 –218.5
17	3.3	424–455	218.5–235
Bottoms	10.4	Above 455	Above 235

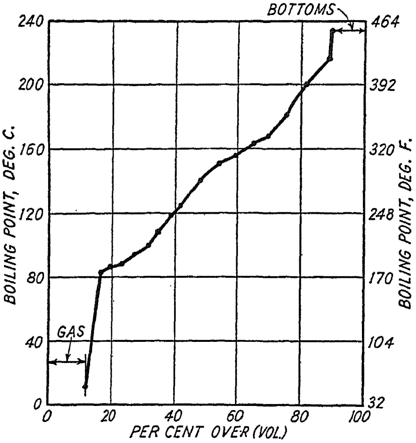

Fig. 56

Acknowledgment

The authors express their thanks to Marvin A. Smith for assistance in constructing and operating the pilot plant.

Summary

A catalytic process has been developed for the conversion of gaseous olefins into gasoline. The catalyst is rugged and active and can be regenerated. The liquid polymer mixture consists essentially of mono-olefins which boil largely in the gasoline range.

Cracked gases containing 17.6, 37.5, 43.1, and 69.7% of propylene and butylenes gave gasoline yields of 3.3, 6.0, 6.8, and 10.9 gallons, respectively, per thousand cubic feet of gas processed.

A commercial polymerization plant is in operation which is producing gasoline at the rate of more than 5 gallons per 1000 cubic feet of cracked gas.

GASOLINE FROM ETHYLENE BY CATALYTIC POLYMERIZATION[1]

This paper describes the properties of gasoline obtained by the catalytic polymerization of ethylene. Ethylene was polymerized in the presence of commercial "solid phosphoric acid" catalyst[2] in a small pilot plant with continuous flow.

This investigation was made under conditions approximating commercial operation for gasoline production, whereas the previous study of this reaction by Ipatieff and Pines,[1] using liquid phosphoric acid as catalyst and long contact time, concerned itself only with the chemical composition of the liquid product.

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[1] Ipatieff and Corson, presented April 15, 1936, in Kansas City, Mo., before the Petroleum Division of the American Chemical Society; Ind. Eng. Chem., *28*, 860 (1936).

[2] Ipatieff, U. S. Patents; 1993512, 1993513, 2018065, 2018066, 2020649 (1935).

Under conditions employed, polymerization was not the only reaction, as evident from the nature of the product, which contained not only polymeric olefins, but also paraffins (aliphatic and cyclic), and aromatic hydrocarbons. Cyclization, dehydrogenation, hydrogenation, and isomerization had also taken place. Such polymerization, we propose to call *conjunct polymerization* in order to differentiate from pure polymerization. It is assumed that a master reaction, in this case polymerization, furnishes the energy necessary for other reactions.

Pilot Plant, Charging Stock, and Method of Calculation

The pilot plant consisted of a vertical catalyst tower, charged with solid catalyst, followed by a stabilizer. The catalyst tube was welded inside a larger tube which was filled with a 50/50 mixture of lead and tin; this metal bath was encased in an electrical heater. Polymerization was carried out at 520 lb./sq. in. gage pressure. The pressure of the incoming ethylene was controlled by an automatic valve, and the pressure on the exit gas from the polymerizer was lowered to the stabilizing pressure of 50 lbs. by another automatic valve. The bottom temperature of the stabilizer was held at 150° F. (66° C.), the top at 70° F. (21° C.). The boiler section of the stabilizer was an electrically heated Jerguson gage glass. Polymer was continuously withdrawn so as to maintain a constant liquid level in the stabilizer.

The charging stock was ethylene of 98% purity, the 2% impurity being mainly ethane. The exit gas was mostly ethylene (about 70%), together with ethane, butenes, isobutane, higher hydrocarbons, and a small amount of hydrogen (about 0.3% by volume). The production of liquid polymer ranged from 0.01 to 0.03 gallon per hour per pound of catalyst depending on the operating conditions.

In calculating the contact times, the free space in the catalyst charge was taken as 63%, the arithmetical mean of the inlet and outlet rates was used as the gas rate, and deviations from the perfect gas laws were neglected.

Polymerization of Ethylene and Characteristics of Ethylene Polymer Gasoline

Table 256 presents run data obtained under three sets of operating conditions. Increasing the temperature 50° F., from 565 to 615° F. (296 to 324° C.), almost doubled the rate of polymer production. Polymer yields are reported on the basis of once-through operation. Recirculation would raise the liquid yield to 90% and better since the only non-polymerizable material in the exit gas was isobutane, 6 to 12%, depending on the operating conditions (see Table 259).

---

[1] Ipatieff and Pines, Ind. Eng. Chem., *27*, 1364 (1935).

TABLE 256

Run Data on Ethylene Polymerization and Properties of Crude Liquid Polymer

		B	
Operating Conditions:			
Hours on Test	288	192	264
Gage Pressure, Lb./Sq. In.	520	520	520
Temp., ° F.	565	615	615
Temp., ° C.	296	324	324
Inlet Gas Rate, Cu. Ft./Hr./Lb. of Catalyst [a]	1.5	2.5	3.4
Contact Time, Seconds	790	420	320
Ethylene Polymerization:			
Conversion to Liquid Polymer, %	73	72	65
Gal./1000 Cu. Ft. of Gas:			
Liquid Polymer	8.0	7.9	7.1
Gasoline [b]	4.7	4.7	4.6
Properties of Crude Liquid Polymer:			
Gr., ° A.P.I. at 60° F. (15.6° C.)	48.8	48.7	48.8
Reid Vapor Pressure at 100° F. (38° C.) Lb.	8.8	8.3	8.1

100-Cc. A.S.T.M. Distillation

Per Cent Distilled Over	° F.	° C.	° F.	° C.	° F.	° C.
Initial B.P.	99	37	108	42	111	44
5	118	48	132	56	142	61
10	134	57	145	63	158	70
20	165	74	177	81	188	87
30	209	98	212	100	220	104
40	272	133	267	131	261	127
50	*352*	*178*	*336*	*169*	*314*	*157*
60	409	209	400	204	364	184
70	462	239	453	234	411	211
80	512	267	503	262	466	241
90	597	314	577	303	534	279
95	639	337	631	333	591	311
End Point	644	340	635	335	625	329

[a] Apparent density of catalyst, 0.9.

[b] Initial boiling point, ca. 106° F. (41° C.); end point 400° F. (204° C.); Reid vapor pressure at 100° F. (38° C.); ca. 6.5 lbs.

Table 257 presents characteristics of 400° F. (204° C.) E.P. steam distilled gasoline from a composite of the crude polymer produced under the various conditions described in this paper. Distillation data for the bottoms from steam distillation are included. Color and gum were satisfactory, and the octane number was 82 (same as crude polymer). The induction period of the uninhibited distillate was only 100 minutes, but 0.025% of inhibitor raised it to 1600.

TABLE 257

PROPERTIES OF STEAM DISTILLED ETHYLENE POLYMER

	Steam Distilled Polymer	Bottoms from Steam Distillation
Gr., ° A.P.I. at 60° F. (15.6° C.)	67.4	26.2
Sp. Gr. at 60° F. (15.6° C.)	0.711	0.897
Color, ° Saybolt	30+	
Color Stability [a]	26	
Gum (Copper Dish), mg./100 cc.	10	
Gum (Copper Dish), mg./100 cc. + 0.025% Wood Dist. Inhibitor	2	
Induction Period, Min.	100	
Induction Period + 0.025% Wood Dist. Inhib.	1600	
Octane No. (C.F.R. Motor Method)	82	
Octane Blending Value [b] (25% in Fuel A-3; C.F.R. Motor Method)		
Reid Vapor Pressure at 100° F. (38° C.), Lb.	6.5	

100-Cc. A.S.T.M. Distillation

Per Cent Distilled Over	° F.	° C.	° F.	° C.
Initial B.P.	106	41	378	192
5	126	52	407	208
10	136	58	421	216
20	151	66	439	226
30	165	74	457	236
40	180	82	475	246
50	*199*	*93*	*492*	*256*
60	222	106	511	266
70	250	121	533	278
80	287	142	561	294
90	325	163	615	324
95	362	183	680	360
End Point	398	203	696	369

[a] Equivalent to 2 hours noon June sunlight.
[b] Octane number of fuel A-3, 44.

Distillation characteristics of the crude ethylene polymer are further illustrated by the Podbielniak distillation data (together with the operating conditions of pressure, temperature, and contact time) listed in Table 258. It is seen that the less severe polymerizing conditions favored the production of a simpler product as shown by the more pronounced plateaus in Curve E. The same tendency had been previously observed in the polymerization of isobutene.[1] The plateau at 150° F. (66° C.)

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[1] Ipatieff and Corson, Ind. Eng. Chem., *27*, 1069 (1935).

corresponds to C_6, whereas that at 410° F. (210° C.) corresponds roughly to C_{12}.

TABLE 258

PODBIELNIAK DISTILLATION OF ETHYLENE POLYMER

	D	E
Polymerizing Conditions:		
Gage Pressure, Lb./Sq. In.	520	520
Temp., ° F.	565	615
Temp., ° C.	296	324
Contact Time, Seconds	810	170

FRACTION No.	BOILING POINT		PER CENT	
	° F.	° C.	Distilled	Over
1	Gas	Gas	3.8	4.0
2	64– 86	18– 30	6.2	0.5
3	86–108	30– 42	3.1	1.5
4	108–129	42– 54	1.9	5.0
5	129–151	54– 66	10.0	14.0
6	151–183	66– 84	3.2	7.9
7	183–194	84– 90	1.8	1.8
8	194–248	90–120	8.0	11.3
9	248–270	120–132	3.2	4.0
10	270–302	132–150	3.5	5.1
11	302–356	150–180	7.7	9.1
12	356–378	180–192	5.1	2.0
13	378–410	192–210	4.1	8.1
14	410–432	210–222	3.6	7.7
15	432–464	222–240	4.8	3.7
16	464–486	240–252	4.0	6.3
17	486–518	252–270	5.1	0.0
18	518–540	270–282	1.7	0.0
19	540–572	282–300	4.2	0.0
20	Bottoms	Bottoms	15.0	8.0

WEIGHT BALANCE OF ETHYLENE POLYMERIZATION

Table 259 presents weight balances for the polymerization of ethylene under two sets of operating conditions, 1400 seconds contact time at 565° F. (296° C.) and 200 seconds at 615° F. (324° C.). The appearance of isobutane and of butene (mixture of n- with smaller amount of iso-) among the products confirms the work of Ipatieff and Pines.[1] It is evident that the relative amount of isobutane production depends upon the operating conditions, 11.6% in E, and 6.4% in F.

Dissolved gas was removed from the crude liquid polymer by stabilization under a Podbielniak column and the composition of this gas was combined with that of the exit gas proper in calculating the weight balances. Liquid polymer includes all components above isobutane. The absence of methane and hydrogen indicates that no cracking took place.

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[1] Ipatieff and Pines, to be published.

TABLE 259

WEIGHT BALANCE FOR ETHYLENE POLYMERIZATION

	E	F
Polymerizing Conditions:		
Gage Pressure, Lb./Sq. In.	520	520
Temp., °F.	565	615
Temp., °C.	296	324
Contact Time, Seconds	1400	200
Liquid Polymer (Crude):		
Gal./1000 Cu. Ft. of Inlet Gas	7.9	7.6
Gr., °A.P.I. at 60° F. (15.6° C.)	47.2	50.2
Conversion of Ethylene into Various Products (% by Weight):		
Ethylene (Recovered)	13.7	18.0
Butenes	0.7	0.8
Isobutane	11.6	6.4
Liquid Polymer	73.7	74.5

CHEMICAL COMPOSITION OF ETHYLENE POLYMER

Table 260 presents refractive indices, densities, and bromine numbers of different fractions of the polymer.

TABLE 260

PROPERTIES OF ETHYLENE POLYMER

Fraction No.	Boiling Point		Per Cent Distilled Over	n_D^{20}	d_4^{20}	Bromine No.
	° F.	° C.				
1	Below 64	Below 18	3.4			
2	64–100	18– 38	5.3	1.3605	0.640	31
3	100–160	38– 71	11.0	1.3808	0.666	55
4	160–190	71– 88	10.3	1.3938	0.686	78
5	190–253	88–123	11.0	1.4108	0.723	96
6	253–311	123–155	10.8	1.4295	0.761	114
7	311–390	155–199	15.4	1.4529	0.787	125
8	390–424	199–218	6.8	1.4690	0.837	113
9	424–527	218–275	19.3	1.4996	0.889	61
10	Above 527	Above 275	6.8	1.5506	0.962	

Table 261 shows the solubility of ethylene polymer in sulphuric acid and characteristics of the residual hydrocarbon. The polymer was shaken with two volumes of 96% sulphuric acid at 32° F. (0° C.), and after standing 15–30 minutes at this temperature, the residual hydrocarbon was separated and redistilled to the original temperature range. The diminution in volume corresponded approximately to the original olefin content. The residual hydrocarbon was olefin-free as shown by the permanganate test. Aromatics first appeared in the 302–392° F. (150–200° C.) fraction, and were present in larger amounts in the higher fractions.

TABLE 261

Solubility of Ethylene Polymer in Sulphuric Acid and Properties of Insoluble Hydrocarbon

Fraction No.	Boiling Point		Polymer		Insoluble Hydrocarbon		
			Solubility in H_2SO_4		Reaction with		
	° F.	° C.	Soluble, %	Insoluble, %	$KMnO_4$	Nitrating Mixture	n_D^{20} ✓
1	86–122	30– 50	21	79	0	0	1.366
2	122–158	50– 70	24	76	0	0	1.376
3	158–212	70–100	62	38	0	0	1.393
4	212–302	100–150	96	4	0	0	1.404
5	302–392	150–200	52	48	0	Weak	1.432
6	392–482	200–250	50	50	0	Vigorous	1.477
7	482–572	250–300	46	64	0	Vigorous	1.502

Table 262 presents analytical data for several fractions of sulphuric acid-insoluble hydrocarbon. The lower boiling fractions (Nos. 1 and 2) were paraffinic, hexane and octane, respectively. The fraction boiling at 340–349° F. (171–176° C.) contained paraffins (cyclic and aliphatic), presumably a mixture of diethylcyclohexane and decane. The 480–487° F. (249–253° C.) fraction was aromatic-cycloparaffinic, presumably a mixture of tetraethylbenzene and tetraethylcyclohexane.

TABLE 262

Properties of Hydrocarbon Insoluble in Sulphuric Acid

Fraction No.	Boiling Point		n_D^{20}	d_4^{20}	Analyses						
					Found			Calcd.			
	° F.	° C.			Mol. Wt.[a]	% C	% H	Formula	Mol. Wt.	% C	% H
1	135–149	57– 65	1.3749	0.658		83.5	16.4	C_6H_{14}	86	83.6	16.4
2	194–198	90– 92	1,3925	0.697	108	84.0	15.9	C_8H_{18}	114	84.1	15.9
3	340–349	171–176	1.4308	0.776	141	84.8	14.8	$C_{10}H_{20}$	140	85.6	14.4
								$C_{10}H_{22}$	142	84.4	15.6
4	480–487	249–253	1.4925	0.897	188	87.4	12.5	$C_{14}H_{22}$	190	88.3	11.7
								$C_{14}H_{28}$	196	85.6	14.4

[a] Determined by freezing point method in benzene.

The fraction boiling at 428–536° F. (220–280° C.) contained cyclic compounds, the evidence being that hydrogenation (nickel catalyst; 100 atmospheres initial hydrogen; 572° F. [300° C.]) converted this fraction (C, 87.1; H, 12.5) into cycloparaffins (C, 85.9; H, 14.4). The product did not react with nitrating mixture.

Information regarding the side chains in this high boiling fraction was obtained by means of a method of destructive hydrogenation (molybdic oxide catalyst; 100 atmospheres initial hydrogen; 572–617° F. [300–325° C.]).[1] Under these conditions, side chains are eliminated as paraffins.

Destructive hydrogenation of 24.5 g. of the 428–536° F. (220–280° C.) fraction yielded a residual gas containing 85.6% of hydrogen and 14.4% of ethane (6.1 g.). The liquid product was stable to the permanganate test but reacted vigorously with nitrating mixture. Table 263 presents constants and analyses of different fractions of the liquid.

TABLE 263

PRODUCTS OF DESTRUCTIVE HYDROGENATION OF 220–280° C. FRACTION OF ETHYLENE POLYMER

Fraction No.	Boiling Point		Aromatics,[a] %	n_D^{20}	Mol. Wt.	Analyses		Products
	° F.	° C.				% C	% H	
1	338–401	170–205	50	1.4681	135	87.8	12.4	$(C_2H_5)_2C_6H_4$ (60%) + C_nH_{2n} (40%)
2	401–437	205–225	50	1.4862	149	88.2	12.0	$(C_2H_5)_3C_6H_3$ (70%) + C_nH_{2n} (30%)
3	437–464	225–240	75	1.4936	161	88.2	11.9	$(C_2H_5)_4C_6H_2$ (90%) + C_nH_{2n} (10%)

[a] Determined by solubility in fuming sulphuric acid (15% SO_3).

ACKNOWLEDGMENT

The authors express their thanks to Marvin A. Smith for assistance in constructing and operating the pilot plant, and to R. C. Wackher for the carbon-hydrogen analyses.

SUMMARY

Catalytic polymerization of ethylene in the presence of commercial "solid phosphoric acid" catalyst yields 4.7 gallons of 82 octane number (C.F.R. motor method) gasoline per thousand cubic feet of ethylene charged (total liquid yield, 7–8 gallons). The operating pressure was 520 lb./sq. in. gage pressure. Two temperatures were employed, 565 and 615° F. (296 and 324° C.). Weight balances calculated for two sets of conditions, (A) 520 lb./sq. in., 565° F. (296° C.), 1400 seconds contact time, and (B) 520 lb./sq. in., 615° F. (324° C.), and 200 seconds show the following conversions: (A) recovered ethylene, 13.7%; butene, 0.7%; isobutane, 11.6%; liquid polymer, 73.7%; (B) recovered ethylene, 18.0%; butene, 0.8%; isobutane, 6.4%; liquid polymer, 74.5%. The liquid polymer contains paraffins, cycloparaffins, olefins, and aromatics.

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[1] Ipatieff and Pines, to be published.

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